



## Indirect methods for determination of dry matter density and basic density of pulp wood

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LABORATORIET FOR BYGNINGSMATERIALER  
Danmarks Tekniske Højskole

BUILDING MATERIALS LABORATORY  
Technical University of Denmark



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Lisbeth G. Thygesen

# Indirect methods for determination of dry matter density and basic density of pulp wood

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The present Minor Subject has been carried out in a cooperation with  
Building Materials Laboratory  
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## **Abstract**

This literature survey presents the state-of-the-art (early 1990s) of potential and existing indirect methods for determination of dry matter content and basic density of wood. For each reviewed method an evaluation of its applicability for pulp wood scaling is given. Near infrared analysis is identified as the single most promising method for this purpose and is therefore given the most thorough treatment.

## Preface

This literature survey is submitted in partial fulfillment of the requirements for passing the minor subject "Non-destructive evaluation". The minor subject forms a part of the requirements for obtaining the Danish Ph.D. degree. The report is written under the guidance of Preben Hoffmeyer, Building Materials Laboratory, the Technical University of Denmark.

The aim of the Ph.D. project is to study and develop methods for determination of dry matter content and basic density of pulp wood. The methods should be applicable in practice for scaling pulp wood upon arrival at the pulp mill. In the nordic countries, the dominant scaling method for pulp wood is presently volume scaling. Apart from providing a more fair scaling, knowledge of dry matter content and basic density would allow a better regulation of the pulping process.

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# Contents

1 Introduction .....	1
2 Indirect methods of measuring pulp wood .....	2
2.1 The indirect measuring principle .....	2
2.1.1 Calibration .....	3
2.2 The variation in dry matter content and basic density in pulp wood and what this variation implies for indirect measurement of these properties .....	7
3 Electrical properties .....	19
3.1 Resistance .....	19
3.2 Dielectric properties .....	20
3.2.1 Factors affecting the dielectric properties of wood .....	21
3.3 Eddy current .....	23
3.4 Piezoelectric effect .....	23
4 Electromagnetic waves .....	25
4.1 Photon - matter interaction .....	25
4.1.1 Micro level approach .....	25
4.1.2 Macro level approach .....	27
4.1.3 Factors affecting the interaction .....	30
4.2 Response from instruments based on electromagnetic radiation .....	30
4.3 Gamma rays .....	31
4.4 X-rays .....	32
4.4.1 X-ray densitometry .....	33
4.4.2 Computed tomography .....	34
4.4.3 Dichromatic photon absorptiometry .....	34
4.5 Fluorescence spectroscopy .....	35
4.6 Near infrared spectroscopy (NIR) .....	36
4.6.1 History .....	37
4.6.2 Instrumentation .....	37
4.6.3 Existing applications .....	39
4.6.4 Parameters influencing NIR measurements .....	40
4.6.5 Evaluation .....	43
4.7 Infrared spectroscopy .....	44
4.8 Microwaves .....	44
4.8.1 Radar .....	46
5 Mechanical waves .....	47

6 Particle absorption/slowing . . . . .	50
6.1 Beta rays . . . . .	50
6.2 Neutron rays . . . . .	50
7 Nuclear magnetic resonance (NMR) . . . . .	52
8 Thermal conductivity . . . . .	57
9 Energy absorption and drilling resistance . . . . .	58
9.1 Energy absorption . . . . .	58
9.2 Drilling resistance . . . . .	58
10 Conclusion . . . . .	60
Literature . . . . .	62
Appendix A	
Multivariate calibration in NIR . . . . .	77
Appendix B	
Absorption bands in the NIR region . . . . .	94



# 1 Introduction

"The determination of moisture content is an important measurement in connection with many operations in the wood based industries. Various physical principles have been used for this purpose, but for most applications ideal, *i.e.* accurate, reliable, fast and inexpensive gauges are still lacking."

[Magnusson *et al.* 1972]

The article from which the above is a citation was written 22 years ago. Sadly, the situation hasn't improved much since then. In the nordic countries, the main scaling method for pulp wood is still volume scaling, although both sellers and buyers agree on the shortcomings of this scaling method. Research has gone on, however, and this literature survey gives the early 1990s state-of-the-art of the main part of (potential) methods for measuring moisture content and basic density of pulp wood. These two variables are considered the two most relevant pulp wood characterizing variables, both for scaling purposes and for optimization of the pulping process. In the report, promising methods are treated in greater detail than more peripheral methods. Prior to the reviews, a basic treatment of indirect methods of measuring pulp wood is given (chapter 2).

In this work, the following terms are used for moisture contents, dry matter contents and densities:

Moisture content (dry basis)	Weight of water per unit weight dry matter.
Moisture content (wet basis)	Weight of water per unit weight wet wood.
Dry matter content	Weight of dry matter per unit fresh (wet) weight.
Basic density	Weight of dry matter per unit fresh (wet) volume.
Specific density	Weight per unit volume, both at a specified moisture content.
Bulk density	Weight per unit volume, both weight and volume including water and air as is (for example for a bucket of chips).
Dry density	Weight of dry matter per unit volume dry wood.

The abbreviation FSP is used for *fiber saturation point*. I am aware of the fact that research using nuclear magnetic resonance (NMR) have revealed that the FSP-based view of water distribution in wood is a simplification, see for example [Hartley *et al.* 1992]. However, many principles for measuring moisture content in wood show a shift in sensitivity at moisture contents traditionally interpreted as the FSP. Therefore the concept is useful for this report.

## 2 Indirect methods of measuring pulp wood

This chapter first describes the indirect measuring principle and calibration. Thereafter an overview is given of Swedish investigations of the variation in basic density and dry matter content in pulp wood. Finally it is considered what this variation means for the evaluation of indirect methods for pulp wood.

### 2.1 The indirect measuring principle

All non-destructive evaluation techniques for the determination of basic density and/or dry matter content of wood are indirect. That is, for all types of instruments described in this report it is necessary to interpret the response signal to get the dry matter content/the basic density. The interpretation is established by calibration of the instrument.

There are, however, "degrees of indirectness". For example, the NMR technique for determination of dry matter content gives response signals that are directly proportional to the number of water-bound hydrogen atoms in the measured volume. Thus, for a given instrument, the NMR response signal depends on only one variable (the amount of water bound hydrogen), and the variable is directly proportional to the amount of water in the measured volume. Among the other extremes, there is the electric resistance through a piece of wood. This will depend not only on the amount of water, but also on the distribution of the water, the type and amount of ions in the water, the frequency of the applied current, the temperature of the wood, the contact between the electrodes and the wood, and other variables. The resistance will not be a linear function of the water content for all moisture ranges. One could say the NMR technique is more selective and less indirect than the resistance technique. The more selective a measuring principle is, and the more simple the relationship is between the response signal and the desired wood property (direct proportionality being the most simple case possible), the more simple it is to establish a calibration, all other things being equal.

To calibrate is to produce a mathematical equation that links the response signal to the desired wood property, so that the property can be calculated from the response signal. Such an equation is called a calibration model. The interrelation between the response signal and the wood property of interest may or may not be understood according to some scientific theory, i.e. the interrelation may be causal or empirical. A causal calibration model implies that one has a theory that explains why and how the instrument works. In addition to the academic satisfaction of this it is advantageous when setting up limits for the range of operation for the instrument. However, refusing to try out a new measuring principle because it should not work according to one's a priori knowledge may shut out principles that work; theories can be incomplete or wrong. In the history of natural sciences it has often been the results that did *not* fit into the existing paradigm that have led to new understandings.

### 2.1.1 Calibration

How is a calibration model made? The basis of a calibration is a set of samples (the calibration set) for which two things are known: The response signal of the instrument in question and the desired wood property measured according to a direct method - the reference method. For dry matter content the reference method could be weighing - drying - weighing, for basic density it could be the water displacement method.

In the most simple case, where the instrument measures according to a highly selective principle, where the instrument response is only one variable (univariate) and where the noise level is low, one can use univariate calibration. That is, plot the reference value against the instrument response, consider which type of function best describes the interrelation, and use least squares (or maximum likelihood) regression to estimate the coefficients of the function in the desired range. If the model is causal, the plot is used for confirmation of the expected type of relationship. In the causal case the expected interrelation will often be linear because instruments normally are constructed to provide linear response within certain limits. In the univariate case the normal approach when facing nonlinearity problems, selectivity problems etc. is to try to pretreat the samples in another way or to adjust the sampling procedure and/or the measuring procedure to secure a higher selectivity and/or a lower noise level. In more complicated cases, where the instrument is less selective, where the response signal is multivariate and/or the noise level is high, these remedies will often be less fruitful than to replace the univariate calibration with a multivariate calibration. That is, the relevant information is extracted from the response signals using Principal Component Regression (PCR), Partial Least Squares Regression (PLSR) or Artificial Neural Networks (ANN) (see Appendix A). If multivariate calibration should have a chance to result in a useful calibration model it is necessary that the response signal hold some information of the desired wood property. However, the response needs not be linear, the method needs not be selective and the noise level needs not be low. Causal univariate calibration models are often based on some assumptions about the sample and/or the measuring situation. When these assumptions are not fulfilled, it is likely that an empirical multivariate calibration model will work better for many prediction purposes. Furthermore, analysis and interpretation of the empirical multivariate calibration might later result in a better understanding of the model and of which factors affect it, thereby turning the empirical model into a new causal model.

From the above description of calibration models it is clear that a single prediction using a calibration model for an indirect method can never be more precise than the reference method used for the calibration. However, normally the point in using an indirect method is not to get more precise single measurements, but to get data faster and cheaper, thereby providing more information at the same cost or providing information where earlier on there was none. In the current applications of indirect measurements in the wood industries, the information gained is used for intensifying process- and quality control.

On the other hand, it would be a simplification to claim that the reference method always gives a better result than the indirect method. In cases where a large deviation is found between the reference and the indirect measurement for a sample in the calibration set, the reference value as well as the indirect value might prove to be erroneous. A special problem arises when the reference method is more coarse or even more indirect than the indirect method. If two or more samples in the calibration set are given the same value according to the reference value, but actually differ in a way that affect the value of the response variable of the indirect method, a good calibration model is impossible to obtain. This problem is often encountered when calibrations for old, well established quality parameters are attempted. For examples of this coarseness problem, see [Martens and Næs 1989 p.134] and [Borgå et al. 1992]. The problems related to obtaining an accurate (unbiased) representation when sampling are the same, regardless of the measuring method (direct or indirect). But because indirect methods normally are both faster and cheaper, the problem of measuring enough samples to get a precise estimate is normally smaller for indirect methods. The same, or even a better precision than that of a single direct measurement of a sample may be reached if more than one measurement is made with the indirect method, since the standard deviation of a number of measurements of the same sample theoretically is reduced by the square root of the number of repetitions (see for example [Box et al. 1978 p.68]). For the calibration of indirect methods there is a further sampling problem if the direct and indirect methods require different sample volumes. If for example only subsamples of the samples can be measured according to the indirect method, one must make sure that these subsamples correctly represent the samples from which they are taken, for example by averaging the response value for a number of subsamples per sample.

What is the maximum number of possible independent calibrations for a given data set? For univariate calibration, the number of independent response variables measured gives the number of possible independent calibrations. When using bilinear multivariate calibration (PCR or PLSR, see appendix A), the upper limit for the number of possible independent calibrations equals the number of PLS/PCR-factors. I.e., normally no upper limit is encountered. When calibrating using neural networks, each independent response variable requires its own specially trained network.

What is a good calibration? Martens & Næs [1989 p.60] list three things, that are needed in a calibration:

- "1. Clear goal formulation, including population considerations.
2. Good validation procedures to ensure predictive ability.
3. Good models, giving sufficient predictive ability and allowing interpretation and model criticism."

Concerning no. 1:

It is an absolute necessity to know the purpose of the calibration. This depends on the measurements, which are to be done later using the calibrated instrument. When

formulating this purpose, one can take start from careful consideration of the following three questions formulated by Johansson [1991 p.3] (the author's translation):

- "1. Why is the measurement to be done?
2. What is to be measured?
3. Which quality is required from the measurement?"

"The measurement" here refers to the measurements to be done later using the calibrated instrument.

The selection of samples for the calibration is crucial. The samples used for the calibration must correctly represent the population from which future samples for measurements using the indirect method are to be taken (the prediction population). If they affect the response signal, also the measuring procedure and the conditions when measuring must be identical, or adjusted for if possible. Concerning selection of samples for calibration in near infrared spectroscopy Næs & Isaksson [1989] and Isaksson & Næs [1990] have treated the subject thoroughly. Their conclusion is that it is important for the predictive ability of the calibration model that the calibration set covers the prediction population as good as possible. Not only concerning the constituent calibrated for but also concerning other constituents affecting the response signal. Whether the distribution of samples should be even or follow the distribution of the prediction population depends on the required precision of the calibration model: if the same precision is required for samples near the edge of the prediction population as for those near the centre of the prediction population, the distribution of samples for calibration should be even. If a higher precision is required for samples near the centre than for samples near the edge of the prediction population, the distribution should be the same as for the prediction population (for example a normal distribution). It is my guess that these guidelines also apply for other methods subject to multivariate calibration.

Under certain circumstances, an alternate way of selecting samples for the calibration may be appealing. It consists of measuring many random selected samples using the fast, indirect method to be calibrated and then see how the samples are distributed with respect to the response signal (if the response is multivariate, one can factor-analyze the data). From the resulting distribution one can then pick a smaller, but well distributed number of samples to be measured by the reference method. These samples will then make up the calibration set. Among others Isaksson & Næs [1990] and Shenk & Westerhaus [1991] have suggested this method. The approach implies that the indirect method is truly non-destructive, i.e. that the reference method can be applied to the samples after they have been measured according to the indirect method. The slower/the more expensive the reference method is, the more relevant is this approach.

Concerning no.2:

Validation of the model implies test of its predictive ability. This is done by using the model to predict the wood property in question for a set of samples from the prediction

population, which has not had any influence on the model (the test set), and for which also the result of a measurement according to the reference method (the actual value) is known. What is mentioned above about the selection of the calibration set also applies for the test set, i.e. the test set should correctly represent the prediction population. The smaller the deviations between the predicted values and the actual values, the better is the predictive ability of the calibration model. While developing the model it may be useful to use cross validation, especially if the number of samples available for the calibration is small. However, only a proper test set validation as described above can provide the data necessary for an evaluation of the model.

Concerning no. 3:

When trying to specify what a good model is, Martens & Næs 1989 [p.60] among other things write:

"A model is a simplified intermediate representation, intended to have, from a specific perspective and for a specific purpose, a structural or functional analogy to some phenomenon in the inaccessible, more complex reality. A good model in calibration is then a model that gives an adequate compromise between simplicity and completeness. The former implies sufficient interpretability; the latter implies sufficient realism and detailed description."

Hence, even if the model is empirical and closely fitted to data, it should preferably show some general structure and not be a "black box".

Martens & Næs [1989 p.60] also stress the importance of knowing the limits to the models application. Preferably, when trying to predict outside the model range, the instrument should identify the sample as an outlier and give a (quantitative) warning. For multivariate calibration with PCR or PLSR this is possible.

In addition to this I will stress the importance of realising that a calibration for a given wood property is never finished. For continuous attainment of reliable data, the calibration model must be maintained, that is verified (i.e. validated using test sets) and adjusted regularly. This is because both the prediction population, the sampling procedure and the instrument itself is likely to change over time. One must not forget the cost of this when considering whether to introduce a new indirect method or not. Further, one must remember that transfer of a calibration model from one instrument to another, or to the same instrument after replacement of some vital part is not a trivial problem for all methods and all instruments. Concerning NIR/NIT, calibration models cannot normally be transferred as is; a new calibration from scratch or at least an adjustment is normally required. Instrument makers in the field are aware of the problem and are beginning to find ways to overcome it (see for example [Workman 1993]).

A thorough treatment of calibration theory is given by Martens and Næs [1989], while Pedersen & Martens [1989] give a summary of the subject.

## 2.2 The variation in dry matter content and basic density in pulp wood and what this variation implies for indirect measurement of these properties

An overview of variations in dry matter content and basic density found in Swedish pulp wood investigations is given in Table 1 to Table 6. Only investigations, which fulfill the following restrictions are included:

1. The basic density must be found using the water displacement method on debarked discs. In most studies included in the overview, knots and decay have been avoided when cutting out discs for determination of basic density. The reported variation in basic density is therefore probably a little lower than the actual variation.
2. Only investigations on delimbed pulp wood are included.
3. Only variations in pulp wood within areas sufficiently small to deliver pulp wood to the same pulp mill are interesting in this connection. Data for the overall variation in pulp wood properties in Sweden are therefore excluded. The largest areas accepted are areas corresponding to scaling associations (VMF's).
4. For investigations where pulp wood has been divided into strata according to origin and/or some wood property, the referred variation includes the variation between strata. The variation reported from such studies is presumably a little higher than in a random sample of pulp wood from the area.

The overview is divided into

- Spruce, which is Norway spruce (*Picea Abies* (L.) Karst),
- Pine, which is Scots pine (*Pinus silvéstris* L.),
- Softwood, which is a mixture of Scots pine and decayed Norway spruce, and
- Birch, which is a mixture of Silver birch (*Betula Pendula* Roth.) and White birch (*Betula pubescens* Ehrh.)

Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (kgm <sup>-3</sup> )	Standard deviation s (kgm <sup>-3</sup> )	Remarks
[Andersson 1983]	Ljusnans VMF	21	15	2	Between piles	no?	419	19.3	S calculated from coefficient of variation
	Dalälvarnas VMF	29	15	2			417	15.4	
	Wermländska VMF	46	15	2			411	19.7	
	Mellansvenska VMF	25	15	2			418	23.8	
	Syd VMF (väst)	14	15	2			422	24.5	
	Syd VMF (öst)	18	15	2			418	23.4	
[Björklund 1984]	Ljusnans VMF	20	10	2	Between logs	no?	410	38	
	Dalälvarnas VMF	20	10	2			414	42	
	Wermländska VMF	2	10	2			423	38	
	Mellansvenska VMF	16	10	2			420	40	
	Syd VMF	23	10	2			424	38	
[Thygesen 1992]	Braviken	12	30	1	Within piles	no	407	41	Strata
		12	30	1	Between piles		407	24	
[Nylinder 1993]	Hyltebruk	40	20-35	1	Between piles	no	395	34.4	Strata
	Ortviken	60	20-35	1			392	19.0	

Table 1. Overview: Swedish pulp wood investigations on basic density variation in Spruce.



Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (kgm <sup>-3</sup> )	Standard deviation s (kgm <sup>-3</sup> )	Remarks
[Andersson 1983] Pine	Ljusnans VMF	15	15	2	Between piles	no?	431	28.0	s calculated from coefficient of variation
	Dalälvarnas VMF	29	15	2			432	19.4	
	Wernländska VMF	29	15	2			424	17.4	
	Mellansvenska VMF	29	15	2			435	17.8	
	Syd VMF (väst)	15	15	2			427	17.9	
	Syd VMF (öst)	16	15	2			431	17.2	
[Björklund 1984] Pine	Ljusnans VMF	20	10	2	Between logs	no?	416	45	
	Dalälvarnas VMF	20	10	2			418	44	
	Wernländska VMF	7	10	2			429	42	
	Mellansvenska VMF	21	10	2			435	46	
	Syd VMF	21	10	2			434	39	
[Nylinder 1993] Softwood	Värö	50	20-35	1	Between piles	no	404	24.6	Strata
	Östrand	60	20-35	1			406	24.1	

Table 2. Overview: Swedish pulp wood investigations on basic density variations in Pine and Softwood.

Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (kgm <sup>-3</sup> )	Standard deviation s (kgm <sup>-3</sup> )	Remarks
[Andersson 1983]	Ljusnans VMF	8	15	2	Between piles	no?	533	21.9	S calculated from coefficient of variation
	Dalälvarnas VMF	21	15	2			510	13.3	
	Wernländska VMF	24	15	2			512	14.3	
	Mellansvenska VMF	21	15	2			510	17.3	
	Syd VMF (väst)	15	15	2			506	12.1	
	Syd VMF (öst)	7	15	2			502	20.1	
[Björklund 1984] (mainly other hardwoods than Birch)	Ljusnans VMF	20	10	2	Between logs	no?	503	34	
	Dalälvarnas VMF	20	10	2			513	32	
	Wernländska VMF	6	10	2			516	33	
	Mellansvenska VMF	20	10	2			516	32	
	Syd VMF	20	10	2			523	34	

Table 3. Overview: Swedish pulp wood investigations on the basic density variation in Birch.

Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (per cent dry matter)	Standard deviation s (per cent dry matter)	Remarks
[Björklund 1988]	Mörum	8	10	3-5	Within log	Yes, <i>Op. cit.</i> p.28	51.8	3.9	
	-	8	10	3-5	Within pile		-	7.3	
	-	8	10	3-5	Between piles		-	6.2	
	Skärblacka	8	10	3-5	Within log		56.2	3.3	
	-	8	10	3-5	Within pile		-	7.2	
	-	8	10	3-5	Between piles		-	5.6	
	Skoghall	8	10	3-5	Within log		52.5	3.7	
	-	8	10	3-5	Within pile		-	6.2	
	-	8	10	3-5	Between piles		-	5.2	
	Norsundet	8	10	3-5	Within log		50.2	2.7	
	-	8	10	3-5	Within pile		-	5.4	
	-	8	10	3-5	Between piles		-	4.6	
	Östrand	8	10	3-5	Within log		52.5	2.7	
	-	8	10	3-5	Within pile		-	6.7	
	-	8	10	3-5	Between piles		-	3.8	
	Obbola	7	10	3-5	Within log		50.6	2.5	
	-	7	10	3-5	Within pile		-	5.5	
	-	7	10	3-5	Between piles		-	3.6	

Table 4. Overview: Swedish pulp wood investigations on the variation in dry matter content in Spruce.

Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (per cent dry matter)	Standard deviation s (per cent dry matter)	Remarks
[Björklund 1988]	Mörum	8	10	3-5	Within log	Yes, <i>op. cit.</i> p.28	46.7	4.3	
	-	8	10	3-5	Within pile		-	4.9	
	-	8	10	3-5	Between piles		-	5.2	
	Skärblacka	8	10	3-5	Within log		49.1	3.4	
	-	8	10	3-5	Within pile		-	5.8	
	-	8	10	3-5	Between piles		-	4.5	
	Skoghall	8	10	3-5	Within log		49.4	3.7	
	-	8	10	3-5	Within pile		-	5.2	
	-	8	10	3-5	Between piles		-	5.3	
	Norrsundet	8	10	3-5	Within log		46.3	3.0	
	-	8	10	3-5	Within pile		-	4.3	
	-	8	10	3-5	Between piles		-	5.9	
	Östrand	8	10	3-5	Within log		47.4	2.8	
	-	8	10	3-5	Within pile		-	5.1	
	-	8	10	3-5	Between piles		-	2.4	
	Obbola	7	10	3-5	Within log		46.9	3.3	
	-	7	10	3-5	Within pile		-	4.7	
	-	7	10	3-5	Between piles		-	3.1	

Table 5. Overview: Swedish pulp wood investigations on the variation in dry matter content in Pine.

Literature reference	Location	No. of piles	No. of logs per pile	No. of discs per log	Level for reported variation	Special formula for standard deviation (volume weighing etc.)?	Mean value (per cent dry matter)	Standard deviation s (per cent dry matter)	Remarks
[Björklund 1988]	Mörum	8	10	3-5	Within log	Yes, <i>Op. cit.</i> p.28	58.0	3.9	
	-	8	10	3-5	Within pile		-	1.8	
	-	8	10	3-5	Between piles		-	2.3	
	Skärblacka	8	10	3-5	Within log		58.1	2.5	
	-	8	10	3-5	Within pile		-	2.3	
	-	8	10	3-5	Between piles		-	2.0	
	Skoghall	8	10	3-5	Within log		58.4	3.5	
	-	8	10	3-5	Within pile		-	1.6	
	-	8	10	3-5	Between piles		-	2.6	
	Östrand	8	10	3-5	Within log		58.3	2.1	
	-	8	10	3-5	Within pile		-	2.1	
	-	8	10	3-5	Between piles		-	2.6	

Table 6. Overview: Swedish pulp wood investigations on the variation in dry matter content in Birch.

Concerning basic density, Table 1 to Table 3 give the general impression that the variation within piles is about twice the variation between piles. For Spruce and Pine it is around 40-45 to 20 kgm<sup>-3</sup>, for Birch it is about 30-35 to 15-20 kgm<sup>-3</sup>. Concerning dry matter content, the picture is more divers. For Spruce (Table 4), the variation within piles is generally somewhat larger than between piles (5 to 3 per cent dry matter). For Pine (Table 5) and Birch (Table 6) there is no general trend in the relationship between the variation between piles and the variation within piles (around 3-5 per cent dry matter).

What are the consequences of the above reported variation for indirect measuring of pulp wood in terms of the number of measurements needed per pile for attaining a given precision? The coefficient of variation  $cv$  of the estimate of the mean value  $\bar{Y}$  of some property  $Y$  is

$$cv = \frac{s}{\bar{Y}\sqrt{n}} \quad (1)$$

where  $s$  is the standard deviation between logs in the same pile and  $n$  the number of measured logs.  $s$  includes the measuring error. From the above tables it is possible to calculate the  $cv$  for given values of  $n$  (or vice versa). These calculations will only be valid if measurements are done according to the direct methods used in the studies. To get an idea of the relationship between  $cv$  and  $n$  if instead an indirect method is used, one must include an estimate of the measuring error of the indirect method. Normally this measuring error is only known relative to the reference method, and only for a test set different from the data for which  $s$  has been found. Henrik Stryhn, statistician at the Royal Veterinary- and Agricultural University has kindly derived me a formula for the estimation of  $cv$  under such circumstances. The formula gives the estimate of what the  $cv$  for a set of samples measured according to a direct method would have been, if the samples instead had been measured according to an indirect method, given that the direct method in question is the reference method used for calibration of the indirect method.

$$cv = \frac{\left[ \frac{s^2}{\bar{Y}^2} + \frac{(\sigma_*^2 - \sigma^2)}{\bar{Y}^{*2}} \right]^{1/2}}{\sqrt{n}} \quad (2)$$

where

$s$  is the sample standard deviation of the data measured according to the direct method, calculated according to the formula

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (Y_i - \bar{Y})^2$$

- $\bar{Y}$  is the mean value of the set of samples measured according to the direct method,
- $\bar{Y}^*$  is the mean value of the set of samples measured according to the indirect method,
- $\sigma$  is the estimate of the measuring error of the direct method and
- $\sigma_*$  is the estimate of the measuring error of the indirect method, calculated according to the formula  $\sigma_* = s_{\Delta}^2 - \sigma^2$ , where
- $s_{\Delta}^2$  is the mean value of the squared differences between the  $Y$ -values according to the direct method and the indirect method, i.e.:

$$s_{\Delta}^2 = \frac{1}{n} \sum_{i=1}^n (Y_i - Y_i^*)^2$$

Formula (2) assumes that the number of logs  $n$  measured from one pile is small compared to the total number of logs  $N$  in the pile. If this does not hold, the right hand side should be multiplied by the correction factor  $(1-n/N)^{1/2}$ . According to Henrik Stryhn [Pers. com. 1993], the correction factor is normally omitted, if it is less than 1/10. The formula also assumes that for both the direct and the indirect method the estimates of  $Y$  are unbiased, that the expected value of the measuring error is zero and that the measuring errors are independent.

With formula (2), I have calculated  $cv$  for different values of  $n$  and vice versa. The results are shown in Table 7 (basic density) and Table 8 (dry matter content). The used values of  $\bar{Y}$ ,  $\bar{Y}^*$  and  $s$  are estimated from Table 1 to Table 6. The same estimate ( $Y$ ) has been used for both  $\bar{Y}$  and  $\bar{Y}^*$ . The used values of  $s_{\Delta}$  and  $\sigma$  are estimates based on the authors experience with direct and indirect measuring of basic density and dry matter content of Spruce. Hence the calculations are purely hypothetical, but constructed to be realistic. In Table 8, the numbers in parenthesis are  $cv$  estimated according to formula (1), when this estimate differs from the estimate according to formula (2).

Description	$s$ (kgm <sup>-3</sup> )	$Y$ (kgm <sup>-3</sup> )	$s_{\Delta}$ (kgm <sup>-3</sup> )	$\sigma$ (kgm <sup>-3</sup> )	Coefficient of variation (in percent) for $n$ equal to					$n$ required for coefficient of variation (in per cent) to be e- qual to				
					1	5	10	20		2	4	6	10	
Spruce	40	400	15	4	10.6 (10.0)	4.7 (4.5)	3.3 (3.2)	2.4 (2.2)		28 (25)	7 (6)	3	1	
	30	400	15	4	8.3 (7.5)	3.7 (3.4)	2.6 (2.4)	1.8 (1.7)		17 (14)	4	2	1	
	50	400	15	4	13.0 (12.5)	5.8 (5.6)	4.1 (4.0)	2.9 (2.8)		42 (39)	11 (10)	5 (4)	2	
	40	370	15	3.7	11.5 (10.8)	5.1 (4.8)	3.6 (3.4)	2.5 (2.4)		33 (29)	8 (7)	4 (3)	1	
	40	430	15	4.3	9.8 (9.3)	4.4 (4.2)	3.1 (2.9)	2.2 (2.1)		24 (22)	6 (5)	3 (2)	1	
	40	400	5	4	10.0	4.5	3.2	2.2		25	6	3	1	
	40	400	30	4	12.4 (10.0)	5.6 (4.5)	3.9 (3.2)	2.8 (2.2)		39 (25)	10 (6)	4 (3)	2 (1)	
Pine	40	420	15	4.2	10.1 (9.5)	4.5 (4.8)	3.2 (3.0)	2.3 (2.1)		25 (23)	6	3	1	
Birch														
	33	510	15	5.1	7.0 (6.5)	3.1 (2.9)	2.2 (2.0)	1.6 (1.4)		12 (10)	3	1	1	

Table 7. Non destructive measurement of basic density of pulp wood. The numbers in brackets in the last two columns are calculated according to Formula (1). See text for further explanations.



Description	$s$ (per cent dry matter)	$Y$ (per cent dry matter)	$s_d$ (per cent dry matter)	$\sigma$ (per cent dry matter)	Coefficient of variation (in percent) for $n$ equal to					$n$ required for coefficient of variation (in per cent) to be e- qual to				
					1	5	10	20		2	4	6	10	
Spruce	Standard	53	3	0.5	12.6 (11.3)	5.6 (5.1)	4.0 (3.6)	2.8 (2.5)		40 (32)	10 (8)	4	2 (1)	
	Low $s$	53	3	0.5	9.3 (7.5)	4.2 (3.4)	2.9 (2.4)	2.1 (1.7)		22 (14)	5 (4)	2	1	
	High $s$	53	3	0.5	16.1 (15.1)	7.2 (6.8)	5.1 (4.8)	3.6 (3.4)		64 (57)	16 (14)	7 (6)	3 (2)	
	Low $Y$	50	3	0.5	13.3 (12.0)	6.0 (5.4)	4.2 (3.8)	3.0 (2.7)		45 (36)	11 (9)	5 (4)	2 (1)	
	High $Y$	56	3	0.6	11.9 (10.7)	5.3 (4.8)	3.8 (3.4)	2.7 (2.4)		35 (29)	9 (7)	4 (3)	1	
	Low $s_d$	53	1	0.5	11.4 (11.3)	5.1	3.6	2.5		32	8	4	1	
	High $s_d$	53	5	0.5	14.7 (11.3)	6.6 (5.1)	4.6 (3.6)	3.3 (2.5)		54 (32)	13 (8)	6 (4)	2 (1)	
Pine	4	48	3	0.5	10.3 (8.3)	4.6 (3.7)	3.3 (2.6)	2.3 (1.9)		27 (17)	7 (4)	3 (2)	1	
Birch														
	2	58	3	0.6	6.1 (3.4)	2.7 (1.5)	1.9 (1.1)	1.4 (0.8)		9 (3)	2 (1)	1	1	

Table 8. Non destructive measurement of dry matter content of pulp wood. The numbers in brackets in the last two columns are calculated according to Formula (1). See text for further explanations.

In Table 7 and 8 the numbers in parenthesis are  $cv$  (column 6) and  $n$  (column 7) estimated according to formula (1), when this estimate differs from the estimate according to formula (2). The results of the calculations according to the two formulas are the same for a precise NDE method (low  $s_{\Delta}$ ). Table 7 and Table 8 show that for the coefficient of variation of the estimate of the pile mean value of basic density or dry matter content to be approximately four per cent, the number of samples per pile should be between five and ten for softwood, below five for Birch. The different examples for Spruce indicate that the within pile variation in relation to the pile mean value is the main source of variation in the coefficient of variation of the estimate of the pile mean. The measuring error of each single measurement has less influence. Therefore the most influential controllable variable for the precision of the estimate of the pile mean is the number of samples taken from the pile. Hence the attainable precision of a non destructive method for measuring average dry matter content or basic density of pulp wood piles is closely connected to how fast the application can perform a single measurement, because this is decisive for how many samples can be taken from a pile when measuring in practice.

When evaluating a method it is not only the attainable precision that counts. Also it's consequences for the (working) environment as well as the price of installing and running the system is important.

## 3 Electrical properties

This chapter describes the use of various forms of interaction between wood and electricity for determination of water content and/or basic density of wood.

### 3.1 Resistance

That the electrical resistance of wood is connected to the water content has been known since the 1920s, and the principle is used in many applications for the wood industries [*Skaar 1988 p.207, Kollmann & Côté 1968 p.184*]. The method is only established for moisture contents below fiber saturation. According to Skaar [*1988 p.211*] the resistance in wood above fiber saturation is mainly determined by the type and amount of ions in the cell-cavity water. Nevertheless research is going on with the aim to extend the range of electric moisture meters to above fiber saturation: Böhner et al. [*1993*] describe a test of a new electrode developed for measuring high moisture contents in softwood, i.e. above 100% on a dry weight basis. For these moisture contents, the deviation between the gravimetrically determined moisture content and the moisture content according to the electrode was up to 30% for individual test specimens.

According to Skaar [*1988 p.219*] no consistent relationship has been found between the density of different woods and their electrical conductivity. According to Andreas Bergstedt, RVAU [*pers. com. 1994*], resistance based moisture meters normally have one empirically found setting per tree species.

When measuring water content, the principle of the method is to measure the resistance through the wood between two electrodes. The electrodes can either be needle-like and driven into the wood, flat plates pressed onto the surface or roller electrodes. Through a calibration a relationship is established between resistance and moisture content. Vermaas [*1975*] lists the factors affecting moisture measurements of wood using resistance meters. From this paper it is clear that the measured resistance depends on several factors beside the moisture content, both wood variables (for example the moisture distribution and grain direction) and experimental variables (for example the applied voltage (the Evershed effect) and the contact resistance between electrodes and wood). Therefore, a calibration model must either include these factors or they must be kept at the same level as during calibration. The most influential factor is the temperature of the wood. James [*1968*] shows data for the relationship between DC conductance, moisture content and temperature for four different North American species. At constant moisture content the conductance increases with increasing temperature. Polarization, ohmic heating and electrolysis alter the resistance during measuring when measuring continuously. Forrer & Vermaas [*1987*] describe the development of a moisture meter in which the influence of these three factors and of temperature are reduced.

According to Skaar [1988 p.221] it affects the measurement whether the current between the two electrodes is parallel or perpendicular to the moisture isostere layers: in the first case (for example pin electrodes parallel to the grain), the layer of highest moisture content through which the electrodes pass tends to dominate the reading, giving an overestimation of the average water content between the electrodes. In the second case (for example flat plate electrodes on either side of a veneer) the layer with the lowest water content tends to dominate, giving too low apparent average water contents.

Since the technique neither makes possible accurate measurements of the water content above the FSP, nor of the basic density, it has no potential for pulp wood.

### 3.2 Dielectric properties

This section is based on [James 1975], [Skaar 1988 p.237-262] and [Lin 1967].

The dielectric properties of a nonconducting material, like wood, characterize the interaction between the material and electric fields. The two interactions of importance are absorption and storage of electric energy in the material due to polarization and the rate in which this energy is lost (dissipated). The first interaction is quantitatively described by the dielectric constant, which is the ratio of the capacitance of a given capacitor with the material as the insulating medium to the capacitance of the same capacitor with vacuum. The more readily the material is polarized, the higher the dielectric constant. Various parameters are used to describe the rate of energy loss. They all refer to the complex dielectric constant, defined as  $\epsilon^* = \epsilon' - i\epsilon''$ .  $\epsilon'$  is the real part of the dielectric constant (defined above) and  $\epsilon''$  is the imaginary part. The complex dielectric constant expresses the total current as a vector sum of loss current in phase with the applied voltage and charging current that is  $\pi/2$  out of phase with the applied voltage, see Figure 1. The angle between  $\epsilon''$  and  $\epsilon^*$  is called the phase angle and is denoted  $\theta$ . The angle between  $\epsilon'$  and  $\epsilon^*$  is called the loss angle and is denoted  $\delta$ . The wider the loss angle, the faster the energy is dissipated. The rate of loss is described by  $\tan\delta$ ,  $\sin\delta$  or  $\cos\theta$ .  $\tan\delta$  is called the loss tangent, or the dissipation factor and is equal to  $\epsilon''/\epsilon'$ .  $\sin\delta$  is called the loss factor by Skaar [1988 p.242], while both James [1975] and Lin [1967] define loss factor as the imaginary part of the complex dielectric constant.  $\sin\delta$  is equal to  $\epsilon''/\epsilon^*$ .  $\cos\theta$  is identical with  $\sin\delta$  but is called the power factor. According to Skaar [1988]  $\tan\delta$  is often called the loss factor because  $\sin$  and  $\tan$  are essentially equal for small angles.

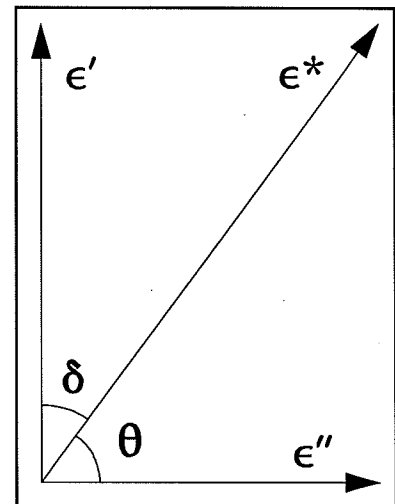


Figure 1. The dielectric constant  $\epsilon^*$  and its components  $\epsilon'$  and  $\epsilon''$ .  $\theta$  is the phase angle,  $\delta$  is the loss angle. Adapted from [Skaar 1988 p.241].

Polarization of wood involves four different mechanisms [Skaar 1988 p.239]:

*Electronic polarization* is caused by displacement of electrons with respect to the nucleus within the atom. It occurs at optical and ultraviolet frequencies (approximately  $10^{14}$  -  $10^{17}$  Hz). *Atomic polarization* is caused by stretching and bending of bonds between atoms of a molecule. It occurs at infrared frequencies (approximately  $10^{11}$  -  $10^{14}$  Hz). *Dipole polarization* (Debye effect) is caused by permanent dipoles such as hydroxyl groups. They rotate in an applied electric field and contribute to the dielectric constant at frequencies sufficiently low to allow the dipoles to follow the changes in the AC voltage ( $40$  -  $10^9$  Hz). *Interfacial polarization* (Maxwell-Wagner effect) is believed to be caused by the accumulation of charged ions at interfaces between different regions within the cell wall. Interfacial polarization occurs at even lower frequencies than dipole polarization ( $<10$  Hz). In addition, James [1975] distinguishes between displacement of individual electrons in an atom, which he calls electronic polarization, and displacement of the atomic nucleus in relation to the group of atomic electrons, which he calls atomic polarization. All polarizations require a finite time to occur, so the polarization never follows a varying electric field exactly. The rate at which a polarization process occurs is expressed quantitatively by the time constant. The time constant is the time required for the polarization under zero field (or the difference between the polarization and its final value under constant field) to decrease by a factor  $1/e$  [James 1975], i.e. to about  $2/3$  of the total rotation they would have in a steady DC field [Skaar 1988 p.239]. The time constant is longest for interfacial polarization (in the order of milliseconds to minutes at room temperature), shortest for electronic polarization (less than picoseconds) [Skaar 1988 p.239]. This variation in time constant is the reason why the dielectric properties depend on the frequency.

### 3.2.1 Factors affecting the dielectric properties of wood

The dielectric properties of wood vary with frequency, moisture content, temperature and density ([Skaar 1988], [James & Hamill 1965], [James 1968 and 1977], [Lin 1967], [Peyskens et al. 1984] and others) and to a lesser degree with mineral content and grain orientation [Lin 1967]. Further, studies by James [1981] show that the electrode design influences the readings and by that the apparent dielectric properties of wood, especially at low frequencies (20-1000 Hz) and at water contents above 7 per cent.

#### *Frequency*

At a given moisture content and temperature the dielectric constant decreases with increasing frequency [James 1975], see Figure 2.

The loss tangent has maximum and minimum values at various frequencies, depending on the temperature and water content [James 1975].

#### *Moisture content*

At a given frequency and temperature the dielectric constant increases strongly with increasing moisture content [Lin 1967], [Skaar 1988 p. 254]. The increase is exponential below FSP, linear above [Lin 1967]. According to Skaar [1988 p.246 + 249], the dielectric constant for

dry wood is about 2-3, while the dielectric constant of water is near 80 below  $10^9$  Hz, decreasing to about 5 above  $10^{12}$  Hz (at 25 °C).

How the loss tangent is affected by the moisture content depends on the frequency (and on the temperature). At room temperature and audio frequencies, the loss tangent increases with increasing moisture content [Lin 1967]. At higher frequencies, the loss tangent shows a peak at a certain frequency, and the frequency for which the loss tangent peaks shifts upward with increasing water content [Skaar 1988 p.257].

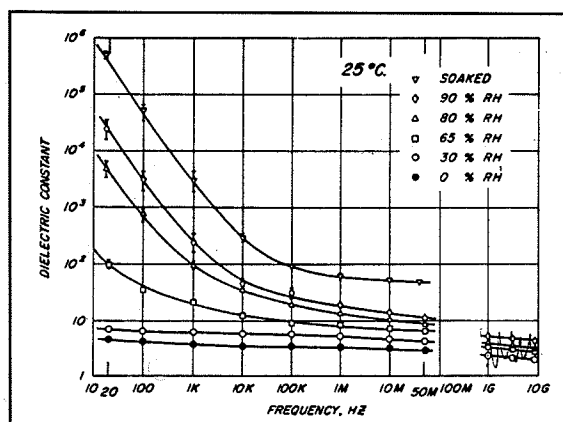


Figure 2. "Dielectric constant of Douglas-fir, field parallel to the grain, at various frequencies and humidities, at 25°C. ... Vertical bars indicate 95 per cent confidence intervals...". From [James 1975].

### Temperature

The dielectric constant increases continuously with increasing temperature [James 1975], and as for water content, the peak in loss tangent shifts to higher frequencies when the temperature increases [Skaar 1988 p.259].

### Density

Both the dielectric constant and the loss tangent increase with increasing density of wood [Lin 1967], [Skaar 1988]. Figure 3 shows the relationship between frequency, water content, specific density and dielectric constant.

### Mineral content

According to Lin [1967] the mineral content of wood affects the loss factor (i.e.  $\epsilon''$ ) at audio frequencies, and the power factor and the loss tangent at radio frequencies. The dielectric constant is reported to vary more with mineral content at audio frequencies than at radio frequencies.

### Grain orientation

Lin [1967] reports that the dielectric values are higher along the grain than across the grain, probably due to a higher degree of alignment of hydroxyl groups along the cellulose axes in the cell walls than across. He also reports a difference in dielectric behaviour between the radial and tangential direction and explains this as a result of the cell wall orientation. James [1981] found no difference in dielectric behaviour between radial and tangential direction.

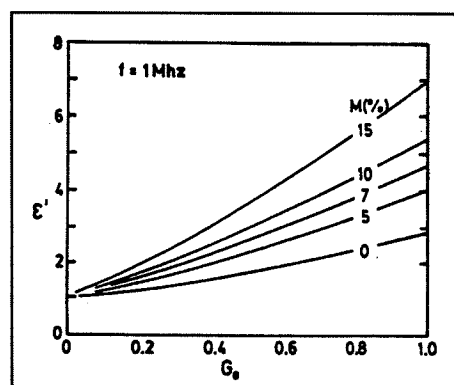


Figure 3. "Curves showing increase of dielectric constant  $\epsilon'$  with increasing wood moisture content and specific gravity (After Uyemura 1960)". From [Skaar 1967].

Dielectric moisture meters based on either measurements of the dielectric constant or the loss

tangent exist, and are often used in the wood industry [Skaar 1988 p. 262]. Measurements of density are also possible. Usually the microwave region is used (see section 4.8).

### 3.3 Eddy current

This section is based on [Madsen et. al. 1988].

When using eddy current to measure the properties of a sample of a material, a coil is placed next to the sample. The electric and magnetic properties of the sample will affect the magnetic field from the coil and determine which signal returns to it (one can think of the coil as the primary coil and the sample as the secondary coil in an imaginary transformer). Two signals are read: one reflects the conductance, the other the phase displacement. The method is mostly used for detecting flaws in metals.

Madsen et. al. [1988] tested the potential of the method as a means to detect decay in wood. He experienced that in the available range from 1 kHz to 1 MHz, the return signal was very weak. For water contents up to approximately 50 per cent, the signal showed a weak tendency towards higher values for higher water contents. At 50 kHz the penetration was 35-40 mm, for higher frequencies approximately 20 mm. The penetration depth did not vary with the water content. Whether the signal depends on the basic density was not tested.

To my knowledge, practically no experience exists concerning eddy current as a technique for measuring water content or density of wood. The findings of Madsen et. al. [1988] suggest that a new test ought to apply a more sensitive instrument and/or another frequency range.

### 3.4 Piezoelectric effect

This section is based on [Knuffel & Pizzi 1986].

Like some crystals, wood exhibit *piezoelectric effect*, i.e., a short lived electrical charge develops on the surface when a pressure is applied to the material. In wood, the piezoelectric effect is caused by shear stresses. When shear stress is applied in the tangential-longitudinal plane, polarization is generated in the radial direction. When shear stress is applied in the radial-longitudinal plane, polarization is generated in the tangential direction. The magnitude of the piezoelectric effect depends on the degree of crystallinity, the density and the water content. The higher the degree of crystallinity, the more polarized will the wood be in the radial direction when subject to a given shear stress. An increase in density gives an increase in polarization in the tangential direction ([Bazhenov 1961 p.71] and Hirai et al. [1968b]) and a decrease in the radial direction [Bazhenov l.c.]. Moisture interferes with the measurements because it raises the speed of the piezoelectric signal (better conductance), but

not the stress wave, whereby the stress wave coincide with the piezoelectric effect. Due to this phenomenon measurements are obstructed at approximately 20 per cent moisture content.

Since piezoelectric effect apparently is obstructed by the moisture in wood already below the FSP, it lacks potential for measuring pulp wood.



## 4 Electromagnetic waves

The greater part of the existing and potential indirect methods for determination of moisture content and/or basic density of wood uses the interaction between electromagnetic radiation and wood. Primarily, the interaction between radiation and matter depends on the relationship between the energy of the incident light quantum (photon) and the association energy of the electron/atom that is hit. The energy of photons is proportional to their frequency, that is inverse proportional to their wavelength. Figure 4 shows the electromagnetic spectrum. The borders between the wavelength ranges are labile, different authors use different borders. The first section of this chapter gives a short description of photon - matter interaction, while types of response from instruments using electromagnetic radiation are discussed briefly in the second section. The rest of the chapter describes the use of various wavelength ranges.

### 4.1 Photon - matter interaction

Two parallel approaches to description of photon - matter interaction exist. The micro level or chemical approach concentrates on the energy transfer from photon to electron/atom/molecule, while the macro or physical approach seeks to describe how radiation is affected by matter.

#### 4.1.1 Micro level approach

If the energy of an incoming photon is large relative to the association energy of the electron/atom/molecule that is hit, the photon is likely to cause photodecomposition. That is, bonds between atoms are disrupted because new particles are formed or because existing electrons are excited by photons. Waves shorter than UV-light (approximately) have this effect on biological material. Three processes dominate in photodecomposition: pair production, Compton scattering and photoelectric absorption (also denoted photo absorption or photoelectric effect). The shorter the wavelength, the more frequent is Compton scattering relative to photo absorption [Lindgren 1973], while pair production dominates for even shorter frequencies [Johns & Cunningham 1971 p.166-168]. According to Johns & Cunningham

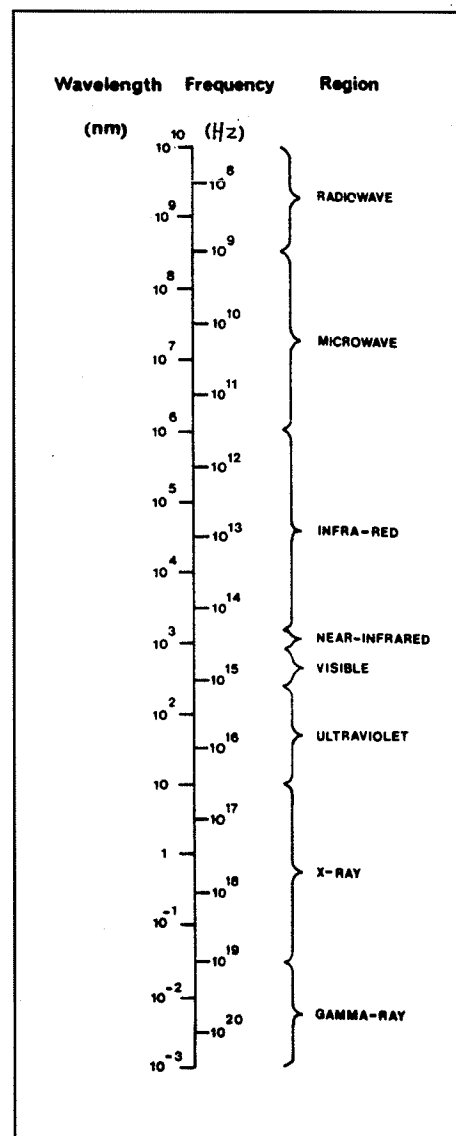


Figure 4. Electromagnetic spectrum. Figure adapted from [Murray & Williams 1987].

[1971 *l.c.*], Compton scattering dominates for photon energies between 200 keV and 5 MeV, while photo absorption dominates for lower energies and pair production for higher energies. In pair production, a photon under influence of the electric/magnetic field near a nucleus changes into an electron and a positron. Formation of the two particles requires 1.02 MeV. Any excess energy goes to kinetic energy of the newly formed particles. In Compton scattering, a part of the energy of the photon is transferred to an electron when they collide. The electron gains enough kinetic energy to depart from its orbital. The photon keeps part of the energy, and leaves from the collision in a new direction and with a longer wavelength. In photo absorption, all the energy from the photon is transferred to the electron, which also in this case leaves its orbital. In all three cases, the emitted particles may again collide with other particles and cause additional radiation and photo decomposition. In addition to the mentioned influence of the energy (frequency) of the radiation, the relative importance of the three processes depends on the atomic number of the elements comprising the specimen. Both pair production and photo absorption increase with increasing atomic number, while the probability for Compton scattering is independent of atomic number [Johns & Cunningham 1971 p.135-171].

If the energy of the photon is of the same order as the association energy of the electron, that is UV and visible light, the photon is likely to cause electron transition from a low energy position to a higher energy position. When the electron falls back to its original position, the excess energy may be emitted as a photon. This process is used in fluorescence spectroscopy. Normally the emitted photon has a longer wavelength than the exciting photon (denoted *Stokes fluorescence*, which is normal for solutions) [Guilbault 1989]. In special cases the emitted photon may have the same wavelength as the exciting photon (denoted *resonance fluorescence*. It never occurs in solutions, but is possible for gases and crystals), or even shorter (denoted *anti-Stokes fluorescence*. It is often observed for dilute gases at high temperatures) [Guilbault *op. cit.*].

Parallel to the three processes described above, photons may be scattered without energy transfer to the electron. This process is described by formulas for Rayleigh scattering (or for Thomson scattering, if the photon energy is much greater than the association energy). Satellite bands to the Rayleigh peaks occur due to the Raman effect (vibrational energy of the exciting photon) [Guilbault *op. cit.*].

If the energy of the incoming photon is less than the association energy, i.e. near infrared or longer wavelengths, the photon will cause vibration or rotation of atoms, groups of atoms in a molecule or whole molecules. This type of energy transfer is treated thoroughly by Murray & Williams [1987]. Where no other reference is mentioned, the rest of this section is based on Murray and Williams [1987].

The covalent bonds between atoms in organic molecules are natural oscillators that vibrate continuously. The frequency depends on the atoms (which elements) and how they are connected. For complex molecules, more than one type of motion is possible: for nonlinear

molecules, there are up to  $3n-6$  different modes of movement of the  $n$  atoms relative to each other (various kinds of stretching and bending). In addition to these vibrations, rotation is also possible. For linear molecules the number of possible vibration modes is  $3n-5$ . Normally the molecule is in the *ground state*, i.e. at the lowest energy level. If the molecule is hit by a photon with the right amount of energy, the molecule will absorb the energy of the photon, thereby being excited to a higher energy level. The wavelength where excitation from the ground state to one of the  $3n-6$  next lowest energy levels occurs is called a *fundamental*. Fundamental absorption normally occurs somewhere between 2,500 and 15,000 nm. If the energy of the photon corresponds to the difference between the ground state and one of the third lowest energy levels or a higher energy level, the molecule is excited to that level instead. The wavelengths where this occurs are called *first overtone*, *second overtone* etc. The first overtone is approximately one half of the wavelength of the fundamental, the second one third etc<sup>1</sup>. The higher the energy level, the fewer molecules will reach it, resulting in lower absorption peaks. For practical, quantitative purposes overtones higher than the third are of little significance. Overtones in the near infra red region relates to fundamentals in the 5-8,000 nm range. These fundamentals correspond to vibration of light atoms with strong molecular bonds, i.e. predominately hydrogen attached to nitrogen, oxygen or carbon [Wetzel 1983]. In addition to fundamentals and overtones, absorption also occurs at *combination bands* and due to *Fermi resonance*. Combination bands are wavelengths where the energy of the photon equals the sum of two or more different vibrations, which then couple. I.e., the molecule is thought to vibrate according to both modes simultaneously. Most combination bands are found between 1,800 and 2,700 nm [Shenk et al. 1992]. Fermi resonance is an effect, which can sometimes be observed, when the wavelength of a fundamental is close to the wavelength of an overtone or a combination involving another fundamental. It results in two absorbancies with the same intensity, both involving both absorptions, over and below the wavelength, where the two signals were expected. The oscillation of covalent bonds depends on their surroundings, such as which molecules are located nearby. The energy states and thereby the wavelength of the photons needed for excitation of a given bond therefore varies. For example, free water and water in wood will not absorb at the same wavelengths. Also there is an effect of the dependency of hydrogen bonds of moisture content and temperature (see section 4.1.3).

#### 4.1.2 Macro level approach

Various sets of equations exist for the interaction between ray and matter. The equation sets apply to different situations.

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<sup>1</sup>

The oscillation of the covalent bonds between atoms is not strictly simple harmonic motion. Therefore it does not strictly obey Hooke's law, the wavelength of overtones (or *harmonics*) being slightly longer than whole number fractions of the fundamental. This phenomenon is called *anharmonicity*.

The Fresnel equations describe the specular reflection and refraction of radiation for a non absorbing material consisting of particles with diameters larger than the wavelength of the incident radiation. In this case, the directions of the radiation leaving the material can be calculated. The Fresnel equations are given by Kortüm [1969 p.6-7].

For densely packed particles, the intensity of remitted radiation will be (almost) independent of the angle of the incident radiation and of the angle of observation. This is called diffuse reflectance. This case is described by the Lambert cosine law [Kortüm 1969 p.28] that relates the remitted radiation flux in a certain direction from a small area to the angle of incidence and to the angle of observation.

When the particles have diameters smaller than or equal to the wavelength, the remitted radiation cannot be split into refraction and reflection. In this case the remitted radiation is collectively referred to as *scatter*. Two theories exist for scatter: Rayleigh scattering [Kortüm 1969 p.75-83] and Mie scattering [Kortüm 1969 p.83-96]. Both concerns single scatter. Single scattering is scattering of (monochromatic) light by particles so far apart that the scatter from one particle does not interfere with the scatter from any other particle. Rayleigh scattering applies to particles (molecules) that are small relative to the wavelength, while Mie scattering applies to isotropic spherical particles.

For multiple scatter, where the particles are so close that interference occurs, only phenomenologic theories exist. The most dominant of these is the Kubelka-Munk theory, treated by for example [Kortüm 1969] and by [Olinger and Griffiths 1992]. Here the central Kubelka-Munk expression is shown in the form used for quantitative analysis:

$$\frac{(1-R)^2}{2R} = \frac{(\ln 10)\mu c}{S}$$

where

- $R$  is the reflectance, infinite sample thickness assumed,
- $\mu$  is the absorptivity (a coefficient, unit:  $\text{m}^{-1}$ ),
- $c$  is the concentration of the absorbing analyte, and
- $S$  is a constant, known as the scattering coefficient.

In arriving at this equation, Kubelka and Munk made several assumptions concerning the sample texture and the radiation flux. The left side of the equation is known as the *Kubelka-Munk function*, and is usually denoted  $f(R)$ . As can be seen, the equation indicates a linear relationship between  $f(R)$  and  $c$ . According to [Olinger & Griffiths 1992] this is not true if the analyte is surrounded by an absorbing matrix or if the absorption bands are strong (fundamentals and/or high analyte concentration).

The Beer-Lambert law describes the loss (attenuation) in intensity of a flux of radiation when passing through a material. Strictly speaking, the Beer-Lambert law is only valid for attenuation of a collimated, monochromatic beam by a uniform absorber [Tiitta et

al. 1993]. However, the law is widely applied, also for situations where these conditions are not completely fulfilled. The Beer-Lambert law is written:

$$I = I_0 e^{-\mu x} = I_0 e^{-\mu_m \rho x}$$

where  $I$  is the intensity of the ray after passage of the material,  
 $I_0$  is the intensity of the incident ray,  
 $\mu$  is the absorptivity (also denoted the linear attenuation coefficient, unit:  $\text{m}^{-1}$ ),  
 $x$  is the thickness of the material,  
 $\mu_m$  is the mass attenuation coefficient, i.e. the absorptivity divided by the density of the material (unit:  $\text{m}^2/\text{g}$ ), and where  
 $\rho$  is the bulk density of the material (unit:  $\text{gm}^{-3}$ )

Thus, if the two intensities, the mass attenuation coefficient and the thickness of a measured specimen is known, its bulk density can be calculated. Use of this approach is called direct scanning densitometry. Both the linear and the mass attenuation coefficient depend on the wave length (energy) of the radiation and on the absorbing material (the elemental composition), but unlike the linear mass attenuation coefficient, the mass attenuation coefficient is independent of the density of the absorber. According to Olson & Arganbright [1981], mass attenuation coefficients for wood are essentially the same, regardless of the chemical composition of the wood, if the radiation energy is above 40 keV. Using a 60 keV source, Malan & Marais [1991] found mass attenuation coefficients ranging from 0.170 to 0.210  $\text{cm}^2/\text{g}$  for a set of wood specimens. Use of direct scanning (regardless of wavelength range) requires that the mass attenuation coefficient for the applied radiation energy is known for the type of specimen measured. The mass attenuation coefficient varies from elemental to elemental and increases rapidly with atomic number. Therefore, though wood consists almost completely of carbon, oxygen and hydrogen in more or less stable proportions, the minuscule but varying content of trace elements such as potassium and magnesium might influence density measurements locally [Pernestål & Jonsson 1992]. The theory of calculating mass attenuation coefficients for wood is treated by Liu et al. [1988].

Other descriptors of ray attenuation are *absorbance*, which is equal to  $\log(I_0/I)$  and *transmittance*, which is equal to  $I/I_0$ .

Figure 5 shows the different kinds of interactions between near infrared radiation

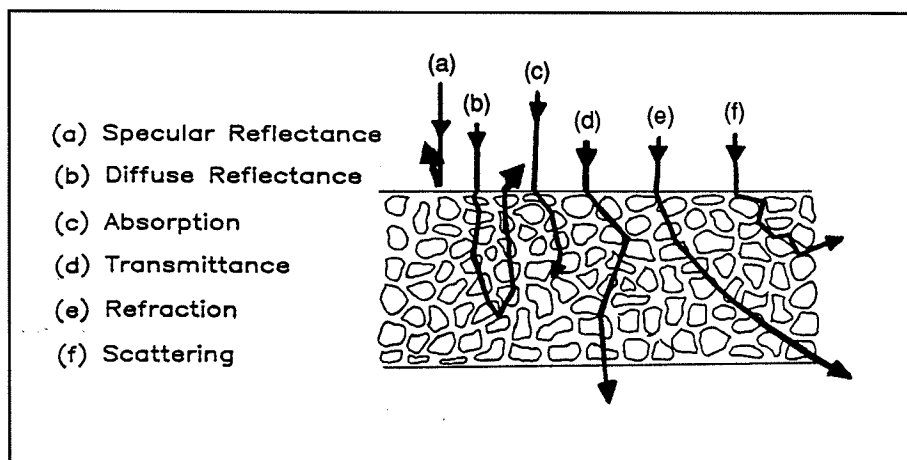


Figure 5. "Interaction of near-infrared radiation with solid particles in a sample". Figure and text from [Shenk et al. 1992].

and a sample consisting of solid particles.

### 4.1.3 Factors affecting the interaction

Apart from the dominant influence of the energy relationships on the ray - matter interaction, a few other factors can in some situations influence the interaction.

For small particles and for wavelengths in the visible and longer ranges, the particle size affects the absorption level. Particles that are large compared to the wavelength will absorb less than particles that are only moderately larger than the wavelength. This is because light that hits the smaller particles will scatter more and will not penetrate so deep. If the particles are even smaller, that is, have diameters of the same size order as the wavelength, the absorption will again increase. This is because the specular reflection will be negligible for such small particles [Kortüm 1969 p.60-73].

The reflectance of small particles also will depend on whether they are surrounded by water or air. If surrounded by water, the particles will reflect more [Kortüm 1969 p.241-243].

Composite bands in the NIR region consisting of multiple overlapping bands will change position with changes in temperature and moisture content due to changes in the relative proportions of the individual bands making up the composite band. The largest variations are caused by changes in hydrogen bonding [Shenk et al. 1992].

For wavelengths causing vibration/rotation, the response also will depend on the state of the sample. Rotation will for example normally only be encountered in the vapour state, because in other states rotations are dampened out by molecule collisions [Murray & Williams 1987].

## 4.2 Response from instruments based on electromagnetic radiation

An instrument based on electromagnetic radiation records one or more characteristics of the radiation after interaction with the sample, often relative to the same characteristic of the incident ray. In cases where the characteristic is difficult to record for the incident ray or where the absolute value of the response variable cannot be obtained, the response is instead recorded relative to the response of a standard sample, measured with the same instrument settings. Figure 5 in the previous section shows various kinds of interaction between near infrared radiation and a sample. The shorter the wavelength, the more dominant is the transmittance. Knowledge of the sample is mainly gained from the transmitted or reflected part of the radiation, because these parts are affected by the sample in other ways than by change

of direction<sup>2</sup>. What is measured is either the bulk loss in energy of the radiation, i.e. attenuation, the change in one or more wave characteristics, or the propagation speed (transmittance only). Attenuation can for example be given as intensity after interaction with the sample relative to intensity of the incident ray (in for example  $\text{J m}^{-2} \text{s}^{-1}$ ). The wave characteristics can for example be wavelength distribution (a spectrum) or one of the dielectric properties (for example phase displacement).

Electromagnetic waves can be used with various degrees of spacial resolution. In the most crude applications, the waves are sent through the material in a few points, and the cumulative attenuation is recorded for each path. This "zero dimensional" approach a priori seems most appropriate for pulp wood. When used for more detailed studies, the attenuation can be measured

- along a profile, using a thin strip of wood, homogeneous in thickness, i.e. a one dimensional approach,
- on a surface (for example a cross section), i.e. a two dimensional approach resulting in achievement of information per unit area (pixel), or
- for each spacial unit (voxel), i.e. a three dimensional approach.

Descriptions of electromagnetic waves for quantitative analysis using univariate calibration illustrate what is mentioned in section 2.1.1 regarding the maximum number of independent calibrations per data set: the number of independent response variables measured gives the number of possible independent calibrations. When the applied radiation is monochromatic and only one characteristic of the radiation is recorded, then only one characteristic of the sample can be subject to calibration (for example moisture content). If another characteristic of the sample also influences the response (for example the basic density), then it must be kept at the same level as during calibration, or measured using another method and corrected for. If the characteristic is recorded for two different wavelengths, or if two independent characteristics of the monochromatic radiation are recorded, then calibrations for two independent characteristics of the sample are possible (for example moisture content and basic density).

### 4.3 Gamma rays

Gamma rays are high energetic, short waves (wavelength range 0.01 to 0.001 nm). Therefore, all applications of gamma rays imply health hazards and environmental risks. All reported uses

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<sup>2</sup>

Some spectroscopes working in the visible and/or near infrared range record a combination of transmittance and reflectance. They are called transreflectance instruments.

of gamma rays for wood density or moisture measurements are variants of direct scanning (see p.29).

The gamma source used most frequently in studies is the  $^{241}\text{Am}$  source, but also the  $^{137}\text{Cs}$ , the  $^{210}\text{Pb}$  and the  $^{55}\text{Fe}$  sources are reported used. For wood with a specific density of  $0.5 \text{ gcm}^{-3}$ , the penetration of gamma rays is between 40 and 400 millimeters [Loos 1965]. Most applications for wood implies use of monochromatic rays and measurement of attenuation. Such applications with only one response signal makes it possible to make calibrations for only one characteristic at a time, i.e. moisture content or density. This technique was used in a zero dimensional approach for clear wood samples by Loos [1961] (specific density or moisture content) and by Malan & Marais [1991] (specific density). Ranta & May [1978] and Laufenberg [1986] recorded profiles of specific density for boards, while Woods and Lawhon [1974] used the technique for acquiring specific density profiles of increment cores. If the sample is measured both in wet and dry condition, both the moisture content in wet condition and the dry density can be determined. Tiitta et al. [1993] and Davis et al. [1993] describe measuring routines based on this approach. As I see it, this type of measurement offers only a slight improvement compared to traditional direct moisture content and density measurement. Moschler & Dougal [1988] give a calibration procedure for a direct scanning, gamma ray densitometer.

The potential of using a dual energy gamma radiation method for simultaneous measurement of moisture content and density of wood was evaluated by Olson et al. [1982]. The evaluation method was error analysis, and three different approaches were examined. Olson et al. conclude that with the present costs and the available technology, the technique does not have industrial potential. A problem in obtaining acceptable errors is the small difference in mass attenuation coefficient between water and dry wood.

The results of Olson et al. [1982] indicate that dual energy gamma ray attenuation has little or no potential for simultaneous measurement of moisture content and basic density. Use of monochromatic gamma rays for determination of either basic density or moisture content requires that the other property is measured using another method and corrected for, as none of the two properties can be assumed to be constant. Approaches using a combination of gamma and neutron rays (see section 6.2) for simultaneous assessment of moisture content and basic density are described by Gibson & Rusten [1964] and by Richesson et al. [1967].

## 4.4 X-rays

X-rays are electromagnetic waves with wavelengths between 0.01 and 10 nm. When used for evaluation of wood, their attenuation when passing through the wood is measured. In most applications, only one feature of the interaction between monochromatic waves and the wood is measured. In these cases, X-rays cannot be used for simultaneous measurement of moisture content and basic density. One must be known to get the other. For evaluation of density or



moisture content of wood, X-rays have been reported used in three ways: for densitometry, for computed tomography (CT) and for dichromatic photon absorptiometry. All applications of X-rays imply health hazards and environmental risks.

#### 4.4.1 X-ray densitometry

X-ray densitometry is the use of X-rays for establishing density profiles. When applied to solid wood, the profiles are often measured on a cross section and used for detailed analysis of density variations within and between annual rings. Two forms of X-ray densitometry exist: photo densitometry and direct scanning densitometry. In both forms, the intensity after passage of a thin wood sample (1-5 mm) is registered. Both forms require samples with a stable water content and homogeneous water distribution.

In photo densitometry, the wood sample is first placed on top of a X-ray sensitive film and exposed to X-rays for a definite time (in the order of hours). Then the resulting grey tone photo negative is analyzed using an optical densitometer. The grey tones are transformed to density values using photos of samples with known density. Photo densitometry for wood was introduced by Polge in the sixties, [Polge 1965] and [Polge & Nicholls 1972]. Improvements to the method are described by Lenz et al. [1976] and by Rudman et al. [1969] while Dupont et al. [1987] specify how to optimize the method. Danborg & Pedini [1990] give a short review of photo densitometry.

In direct scanning X-ray densitometry, the transmitted rays are recorded directly using detectors. When the thickness of the sample, the incident flux and the mass absorption coefficient of the sample is known, its density can be calculated using the Beer-Lambert law (see p.28). Direct X-ray densitometry is of a later date than photo densitometry. Direct scanning X-ray densitometry is described by Cown & Clement [1983], Hoag & McKimmy [1988] and Jonsson et al. [1990]. The system described by Cown & Clement uses X-ray radiation from a radio active isotope ( $^{55}\text{Fe}$ ), while the system developed by Johnson et al. uses an X-ray tube.

For a possible pulp wood application, X-ray densitometry is not relevant. The method gives the specific density at a preset water content, but neither the water content nor the basic density can be measured. Furthermore, the careful sample preparation and conditioning is too time consuming, also for the direct approach.

#### 4.4.2 Computed tomography

This section is based on [Lindgren 1992].

Computed tomography (CT), also denoted computed axial tomography (CAT), is the computation of two-dimensional sectional views of three-dimensional bodies. In X-ray CT the density is computed for small elements (*voxels*) of the body (typical voxel side lengths are a few millimeters). What is recorded is the *CT-number*, i.e., the linear attenuation coefficient  $\mu_x$  normalised by the linear attenuation coefficient for water  $\mu_{\text{water}}$ :

$$CT\text{-number} = 1000 \cdot \frac{\mu_x - \mu_{\text{water}}}{\mu_{\text{water}}}$$

A *CT-number* of -1000 corresponds to air density, while a *CT-number* of 0 indicates water density. A calibration model is established between *CT-number* and density using calibration objects with known density. Lindgren [1992] presents a linear calibration model for this. The model is not validated. For wood, it is a problem to measure reference densities of the small volumes that new CT-scanners offer (voxels with side lengths in the order of  $\mu\text{m}$ ).

CT can also be used for indirect determination of water distribution. This implies measurement of the density distribution twice for each sample: in wet condition and as oven dry. After correction for shrinkage, the two images can be subtracted from each other, and the difference in density is due to water. If the average moisture content of the sample when scanned in wet condition is known, the recorded density differences can be transformed to moisture contents. Determination of average moisture content is also possible. Calibration then requires determination of average *CT-number* for samples with equal density but conditioned to different moisture contents. Lindgren [1992] shows calibration models that link water content to average *CT-number* for two different density levels. Each model has a linear term for moisture content below FSP and one for moisture content above FSP. The models are not validated.

CT offers detailed investigation of wood structure (annual rings, knots), wood density- or moisture content distributions in solid wood. If one is only interested in log means or pile means, as is the case for pulp wood, the method is not adequate. It would be "to use a sledge hammer to crack a nut".

#### 4.4.3 Dichromatic photon absorptiometry

Dissing & Nylinder [1981] tried dichromatic photon absorptiometry for determination of the fractional water content of chips. They define the fractional water content as the water content on a fresh weight base. The method consists of simultaneous (or consecutive) measurement of the attenuation of X-ray photons with two different energies. One photon energy per constituent element is needed, but for this application wood can be treated as a compound of

only two elements: dry wood and water. If the mass attenuation coefficient is known for each element and photon energy, the fractional water content can then be calculated through the set of equations presented by Dissing and Nylinder [*op. cit.* p.8]. The equations are based on Beer-Lambert's law.

Dichromatic photon absorptiometry might be a possibility for water content determination of pulp wood.

## 4.5 Fluorescence spectroscopy

This section is based on [Guilbault 1989].

Fluorescence is light emitted by molecules during the period in which they are excited by photons. Photons in the ultraviolet and visible regions (about  $10^1$  to  $10^2$  nm and  $10^2$  to  $10^3$  nm) of the electromagnetic spectrum have energies that may cause electronic transition and by that fluorescence. More energetic photons (shorter wavelengths) are more likely to result in photodecomposition than fluorescence, while less energetic photons only have energy enough to result in vibrational or rotational transitions, which result in much weaker fluorescence. A molecule will only give fluorescence if the energy of the photons matches the gap between two of its energy states. If no adequate gap exists, the molecule will not show autofluorescence or primary fluorescence. However, addition of reagents, which for example change the specimen's pH can change some of its components in such a way, that they become fluorescent. Fluorescence accomplished in this way is called secondary fluorescence. Lignin is autofluorescent, while secondary fluorescence from cellulose might be achieved by use of the chemical Calcofluor [Munck 1993 *pers. com.*] (concerning Calcofluor, see [Munck 1989 p.19]). The fluorescence normally observed from solutions is reemission of less energetic photons, than the emitting photons, i.e. photons with longer wavelengths. Fluorescence is described by three characteristics:

1. The quantum yield (also denoted the quantum efficiency), which is the ratio of the total energy emitted per quantum of energy absorbed. The higher the quantum yield, the greater the fluorescence of the compound.
2. The excitation spectrum, which is the relative efficiency of different wavelengths of exiting radiation to cause fluorescence.
3. The emission spectrum, which is the relative intensity of radiation emitted at various wavelengths.

Theoretically, the shape of the excitation spectrum should be independent of the wavelength at which the fluorescence is measured and it should be identical with the shape of the

emission spectrum. Because of instrumental artifacts, this is seldom the case. The three characteristics are normally very specific (i.e., two different substances seldom have the same three characteristics).

In a fluorometer light is emitted from a source through a filter to the sample. The wavelength to be measured is selected by a second filter placed at a 90° angle from the incident optical path. After passage through this filter the selected light is intercepted by a detector. The output from the detector is an electrical current proportional to the intensity of the fluorescent energy. In more expensive instruments the filters are replaced by prism or grating monochromators. The bent construction assures that only fluorescent light reaches the detector, while the transmitted part of the incident light continues straight forward. This is a factor that contributes to the high sensitivity of the fluorometer. The response signal from the instrument can either be used for imaging purposes, qualitative analyses or quantitative determination of the constituents. In the last case calibration may be either uni- or multivariate.

The main disadvantage of the method is its serious dependence on environmental factors such as temperature and pH. Another is the risk of photochemical changes in the compound being measured. Further, there is the risk of what is called quenching. This is a reduction of fluorescence by a competing deactivating process resulting from the specific interaction between a fluorophore and another substance present in the system. Quenching can be caused by oxygen, impurities, high temperatures and high concentrations of the fluorophore. To avoid concentration quenching in solutions, the solution should absorb less than 5 percent of the exciting radiation.

The present technique is for use in laboratories, while to my knowledge instruments for use on-line in the industry do not yet exist.

Concerning pulp wood, the method is not appropriate in the present form. It is too dependent on environmental factors, which are not easy to control in a practical measuring situation. It also implies careful sample preparation, perhaps even chemical treatment of the wood. Only if an application is found in which these problems are dealt with, the method might have a potential. A multivariate approach, where the most influential environmental factors are also measured and included in the calibration model might solve the first problem.

## **4.6 Near infrared spectroscopy (NIR)**

Near infrared reflectance spectroscopy (NIRR) and near infrared transmission spectroscopy (NIT) uses wavelengths in the 700 to 3.000 nm range. Because of the presumably high potential of the NIR measuring principle, it is treated in greater detail than any other method mentioned in this report.

### 4.6.1 History

As mentioned in section 4.1.1, the absorption bands observed in the near infrared range are overtones and combinations. A list of absorption bands in the near infrared range is given in appendix B. Overtones and combinations are weaker than the fundamentals in the mid infrared region, and thermal-sensitive devices able of detecting infrared bands cannot detect in the near infrared range. Therefore it wasn't until photoelectric detectors were invented that measurements in the NIR range became possible [Osborne 1981]. The first attempts to use NIR for analysis were carried out in the 1950s [Wetzel 1983]. In the 1960s commercial single-purpose dual-wavelength NIR diffuse-reflectance production line instruments appeared [Wetzel *op. cit.*]. For an example for paper, see [Beutler 1965]. The instrument presented in that article uses the wavelength 1940 nm for moisture detection and the 1800 nm wavelength as a reference. In the late 1960s Norris and co-workers recognized the potential of multiwavelength NIR for quantitative analysis of agricultural products [Wetzel *op. cit.*]. This work led to commercial multiwavelength filter instruments, in USA in the 1970s, in Europe in the 1980s [Wetzel *op. cit.*]. In filter instruments, the different wavelengths are generated by letting white light through a filter that permits only light of a certain wavelength to pass. Filter instruments can have from two to twenty filters, which sequentially are placed in front of the white light beam. A late branch of NIR instruments development consists of scanning instruments, which generate and measures at up to several hundred (neighbouring) wavelengths. The output from a scanning instrument is a spectrum.

Filter instruments are normally calibrated using multiple linear regression, while calibration of scanning instruments requires multivariate calibration. An overview over multivariate calibration in NIR is given in Appendix A.

Reviews on NIR history are given by Wetzel [1983] and by Burns and Margoshes [1992], who give references to other review articles on NIR.

### 4.6.2 Instrumentation

The basic configuration of NIR/NIT instruments is shown in Figure 6. The light source is often a tungsten-halogen lamp or near infrared emitting diodes (NIR-ED's), in which case no monochromators are needed.

Most currently available filter instruments use tilting/rotating filters, see [Polesello & Giangiacomo 1982], [Williams 1987a] and [Workman & Burns 1992] for examples. Scanning instruments traditionally use grating monochromators, but according to [Kemmeny 1992a] two new technologies for generating multiple wavelengths are in progress: diode arrays and acoustooptical tunable filters (AOTF). Both technologies are inherently faster because the wavelengths are selected electronically instead of mechanically.

NIR-ED's can be used in (at least) two different ways: either as sequential emitters (i.e., one diode emits at a time) or as parallel detectors, i.e., white light is sent through (or at) the sample and the intensity of the transmitted (reflected) light is detected simultaneously using one diode per wavelength. The serial approach is used in the instrument design described by Hyvärinen et al. [1992], while Stark [1992] describes the parallel approach. According to Hyvärinen et al. [op.cit.], the presently available ED's are best suited for use in the visible region and the lower end of the NIR wavelength region. They also mention that the wavelength resolution of the light emitted from ED's is relatively poor. Their instrument corrects for this.

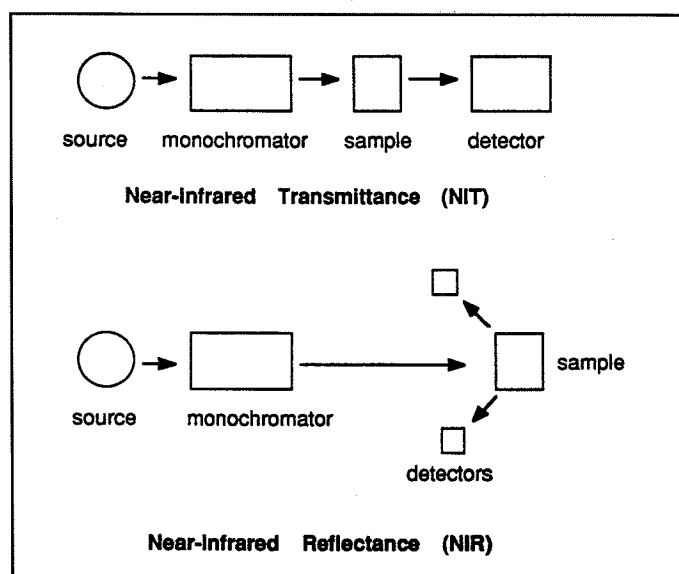


Figure 6. Basic NIR/NIT instrument configurations (from [Workman & Burns 1992]).

In AOTF-based spectroscopy, white, polarized light is sent through a  $\text{TeO}_2$  crystal, through which an ultrasonic wave propagates. The wave is induced by a piezoelectric acoustic transducer (made from  $\text{LiNbO}_3$ ). The light beam will be split three: two identical polarized, monochromatic beams and one beam of unaltered white light. The wavelength of the monochromatic beams is regulated by the frequency applied to the transducer. Normally radio frequencies are used. The AOTF technique is described by Kemmeny [1992a and b] and by Pickuth et al. [1992]. According to Kemmeny [1992a], the wavelength resolution of AOTF instruments is equal to that of instruments based on grating monochromators, while the long-term wavelength repeatability is better.

The detector is normally a semiconductor such as PbS, Si or InGaAs. PbS detects in the range from about 600 up to about 3000 nm (normally the 1200 to 2400 nm is utilized). PbS is a relatively slow detector. Si is faster, but is only capable of detecting up to about 1000 nm. InGaAs can be used for scanning from approximately 800 to 1600 nm. An InGaAs detector normally has a higher signal to noise ratio than a PbS detector (i.e., it is more sensitive) and is relatively quick [Claus Borggaard, Danish Meat Research Institute, pers. com. 1994].

As previously mentioned, it is normally the reflectance relative to a ceramic disc which is measured in NIR. In this case it is not necessary that all light reflected from the sample reaches the detector. However, some instruments are designed to measure the absolute reflectance and/or to measure weak reflectance. This is achieved by encapsulating the sample and the detector(s) in an integrating sphere (not shown in Figure 6). Generally it is

advantageous to collect a maximum of the diffusely reflected radiation. This will give a stronger signal and more directions will be represented and averaged [Wetzel 1983]. The first gives less susceptibility to instrument noise, the second gives less susceptibility to sample texture.

In addition to the NIR-Ed's and the AOTF techniques mentioned above, novel instrument development includes separation of the NIR/NIT instrument from the sample point by use of fiber-optics [Kemmeny 1992a]. Thereby the wear on the instrument is reduced, because it allows placing the instrument in a more friendly environment (for example an environment with less dust, moisture and vibrations). Fiber-optics are also used for reducing installation costs (fewer instruments necessary) and for eliminating the calibration-transfer problem (see p.6). This is achieved by letting one instrument receive signals from several sensors (multiplexing). Furthermore, work is carried out on making NIR instruments smaller (handheld), more robust (no moving parts) and with better wavelength resolution. In addition to these hardware refinements, research and development in this field concentrate on tuning existing calibration techniques, inventing new multivariate calibration techniques, improving the possibilities for calibration transfer and refining the software for multivariate calibration.

A new NIR scanning instrument costs approximately 500,000 to 700,000 DKK, depending on which technology it uses. A NIR instrument measuring at a few wavelengths can be purchased for approximately 20,000 DKK, while a filter instrument with 15-20 filters costs approximately 200,000 DKK.

Overviews over NIR instrumentation are given by McClure [1987] and by Workman & Burns [1992], who among other things give a word list and a list of distinguishing characteristics of NIR instrumentation, which can be useful when purchasing a NIR instrument. Williams [1987a] outlines the design of a considerable number of different commercial NIR/NIT instruments, while the latest (1992) technical improvements are described in [Kemmeny 1992a].

#### 4.6.3 Existing applications

As mentioned in section 4.6.1, multiple wavelength NIR determination was introduced around 1970. It is now a well established technic in the agricultural, the food and the pharmaceutical industries. The main use is for quantitative determination of constituents in raw materials, intermediate and final products. The information gained allows for tight, automatic process and quality control. The technic is constantly improving, and new application areas are found. Examples of applications are given in [Burns & Ciurczak 1992] and in [Anonymous 1993a].

With regard to wood, NIR based on a few wavelengths is in use for moisture determination on chips during chip board manufacturing, [Andersson & Yngvesson 1992] and

[Pedersen et al. 1993]. Research with promising results is going on concerning the potential of NIR in the pulp industry ([Birkett & Gambino 1989], [Easty et al. 1990] and [Wallbäck et al. 1991a and b]) and in chip board manufacturing for characterization of resin/chip mixtures, [Kniest 1992] and [Niemz et al. 1992]. Borgå et al. [1992] investigated the use of NIR for revealing storage time and water quality of wet-stored timber, while Hagman [1992] tested NIR for classification of wooden surfaces. Nair & Lodder [1993] used NIR for identification of solid wood. Also basic research on application of NIR to wood is carried out ([Tsuchikawa et al. 1992] and [Schultz & Burns 1990]). Pedersen et al. [1993] explored NIR for measuring dry density of small clear wood specimens and obtained promising results. Concerning basic density, the results from a pilot study carried out by the author are encouraging, but further development is needed (results are to be published separately).

Thus, NIR measurement of moisture in wood is already established, while NIR measurement of basic density requires some development. NIR measurement of wood constituents (cellulose, lignin) is possible.

#### 4.6.4 Parameters influencing NIR measurements

A number of parameters concerning the sample and how it is presented to the instrument affect the response from a NIR instrument. This section sums up the influence of the more important ones. Most parameters can be adjusted for by multivariate calibration and/or preprocessing. Nevertheless it is important to know of their influence also when scanning instruments are used, especially to avoid systematic differences between calibration samples and the prediction population.

##### *Moisture*

Scattering of light is influenced by whether the sample is wet or not. If water (or water vapour) replaces the air in and around a sample, the scattering will decrease, and the reflectance will increase (see section 4.1.3).

Generally, the predictive ability of NIR calibrations is lower for wet samples than for dried [Reeves 1992]. Water causes smoothening and broadening of peaks as well as peak shifts. Williams [1987b] mentions that constituents of biological origin (for example proteins) are likely to be hydrated to different degrees if the moisture content varies. This could be the reason for some observed peak shifts. Abrams et al. [1988] further suggest that solvents damp vibrations of solutes. Also water is reported to alter composite bands ([Shenk et al. 1992], see section 4.1.3). However, Reeves et al. [1989] did not find an unambiguous negative effect of water on SMLR calibrations for constituents of silage, when comparing between calibrations based on dry and wet samples. The reason for this is perhaps that some of the constituents calibrated for are volatile and evaporated during drying, while all reference chemical analyses were carried out on undried subsamples.



### *Temperature*

The influence of temperature on MLR calibrations for protein and moisture content in wheat was investigated by Williams et al. [1982]. For some filter instruments, the effect was negligible. A particular instrument gave 0.1 per cent differences in protein content per 5 °C (temperatures from -10 to 45 °C). They found that the difference between filter instruments could be subscribed to the use of different wavelengths, i.e. the absorption at some wavelengths is more affected by temperature than at others. They further concluded that protein calibrations unsensitive to temperature changes tended to be more sensitive towards other parameters such as moisture content. Delwiche et al. [1992] studied the effect of temperature on water absorption bands (1400-1500 nm and 1900-2000 nm) of transmittance spectra of starch and cellulose. They found that the bands shifted slightly towards shorter wavelengths as the temperature increased from -80 to 60 °C. According to Kemmeny [1992a] the effect of temperature on NIR measurements is due to the effect on hydrogen bonding, leading to peak shifts of composite bands.

### *Absorbing matrix*

A matrix absorbing at the same wavelength as the analyte can be a problem in NIR if univariate calibration and the Kubelka-Munk function (see appendix A) is used. It will lead to a concave relationship between the K-M function and concentration rather than a linear [Olinger & Griffith 1988].

### *Sample movement*

The possibility of letting the sample move, for example on a conveyor, while NIR measurements are taken is considered by Kemmeny et al. [1988] and by Kemmeny [1992a]. These papers demonstrate that if the readings of consecutive measuring points vary and are uncorrelated, a large number of fast averaging is needed if a reliable estimate of the mean is to be found. However, if all measuring points are fully correlated, no improvement with an increasing number of samples will occur (this of course applies to all replications of measurements, not only moving samples). If the scanning rate (or rate of change between filters) is low compared to the speed of the moving sample, large fluctuations in the spectra can be expected. The reason for this is that different wavelengths comprising the same scan will be reflected from different parts of the sample. This will enhance the need of averaging many spectra.

*For samples consisting of particles, two additional parameters influence the measurement:*

### *Particle size*

Within certain limits for particle size relative to the wavelength of the incident light, the size and shape of the particles and the variation in these two parameters among the particles

influence the scattering of the light. Scattering diminishes with increasing mean particle size. Light will therefore penetrate deeper into a sample consisting of larger particles, and the reflectance will be lower. The effect on NIR spectra is thus a baseline shift. For NIR, an effect of particle size is seen for particles up to about one or two millimeters in diameter. For larger particles specular reflectance overrules the effect of particle size. I guess this is the reason why Reeves and Blosser [1991] did not find any effect of particle size for ground silage samples up to 9.5 mm in size. The effect of particle size is most pronounced at wavelengths at which the sample absorbs strongly [Norris & Williams 1984]. Low energetic photons (long wavelengths) will be absorbed to a higher degree than high energetic photons (short wavelengths), all other things being equal. Therefore differences in particle size between samples give both baseline shifts and differences in slope. A preprocessing method aimed at eliminating these effects is the multiplicative signal correction (MSC), which is described in appendix A. Norris and Williams [*op.cit.*] found that MLR calibrations based on samples with a high in-sample variation in particle size gave better predictions than calibrations based on more homogeneous samples. Their results are for wheat particles in the 0.35 to 1 mm range. Olinger & Griffiths [1993] also found the above mentioned baseline shifts for NIR spectra of sucrose particles. No band distortions were found.

Particle size influences how many different parts of a sample are covered by a single NIR measurement, i.e. particle size influence representation. Smaller particles allow a greater variation to be presented in a given area, but at the same time smaller particles give more shallow penetration. The general rule of thumb in NIR analysis is *the smaller particles, the better calibrations can be expected*. However, Reeves & Blosser [1991] found that for calibrations for silage samples, finely ground samples did not give better calibrations for dry matter content than coarsely ground samples, when both types of samples were measured once. Calibrations for ground samples were marked better than for intact samples, also when three subsamples per intact samples were measured. They found essentially no difference between using one, two, three or the average spectra per intact sample. From this they conclude that the problem with intact samples is related to the particle size itself (by which I guess they refer to the high specular reflection from large particles), not a representation problem. They therefore deduct that for the instrument configuration and calibration procedures used, intact samples, even when measured many times will always result in poorer calibrations than ground samples. I doubt that this conclusion is fully justified. The standard deviation in dry matter content for the samples they used is approximately 12 per cent, the mean value approximately 50 per cent (alfalfa and alfalfa with grass silage). If the in-sample standard deviation is assumed to be of the same order as the between-sample standard deviation (which is not unrealistic for biological material), this means that approximately 370 subsamples should be measured per sample, if the confidence interval for the estimate of the mean value should be approximately five per cent of the mean value (formula from [Rudemo 1979 p.182] used). To conclude anything about the effect of representation based on one to three subsamples per sample therefore seems inappropriate.

### *Packing density*

The packing density affects the structure of the surface of the sample, and thereby its optical properties [Williams 1987b]. Differences in packing densities between samples should therefore be avoided, for example by using samples of approximately the same weight. According to Williams [op.cit], high bulk densities are generally easier to reproduce than low bulk densities. He recommends sample grinding to allow more dense packing. For measurements in the mid infrared area, Yeboah et al. [1984] found that band intensities became more reproducible when powdered samples were compressed, as long as the pressure applied was too low to cause the samples to become transparent.

I have found no literature explicit commenting on the relationship between sample bulk density and NIR penetration. If the penetration depth equals a certain number of particles, as described by Olinger & Griffith [1988], low bulk densities theoretically should lead to deeper penetration. High bulk density presumably results in a more even surface, which leads to more specular reflectance.

### **4.6.5 Evaluation**

NIR determination is currently the most promising technique for solving the problem in question. It is a fast method, and it is already well established in other fields, i.e., presumably a pulp wood application would imply less "teething trouble" than a newly introduced measuring principle. Because there is a market pull for further use of NIR, the technique is rapidly improving. Further, the method a priori must be considered robust to changes in scaling, especially if scanning instruments are used. That is, it seems likely that a new prize setting quality parameter (for example mean cellulose content) wouldn't need new instrumentation, but could be introduced by adding another calibration (or replacing an existent). This advantage is not exclusive to NIR, but applies to all methods calibrated by multivariate calibration.

The three main problems that must be considered prior to an introduction of NIR to scaling purposes are

- \* *Representation.* How many samples are needed? Section 2.2 in this report in part answers this question.
- \* *Presentation.* How should the wood be presented to the instrument? Should the instrument come to the wood (for example surface measurements or via a probe in drilled holes) or should samples be taken to the instrument? In the last case: which form should the samples have (dust, shavings, chips)?
- \* *Calibration.* Calibration is a matter of reliability and trust. How to ensure continuous top quality calibration maintenance?

In addition, there is, as for any other measuring principle various technical and practical problems to consider in connection with applying NIR.

## 4.7 Infrared spectroscopy

Infrared radiation, i.e. radiation in the 3000 to  $10^6$  nm range, is widely used in analytical chemistry for qualitative and quantitative analysis using spectroscopy. Though faster than "wet chemistry" methods, IR normally requires time consuming pretreatment of the samples. Like NIR, IR can be applied either in transmittance or reflectance mode. Normally the spectra are mathematically treated using derivation or deconvolution in the Fourier space (FTIR) (see *McClure [1992]* and *[Mark 1992a]* for an introduction to Fourier transforms in spectroscopy). This treatment enhances the resolution of the spectra, i.e., moderately overlapping and noisy peaks can be extracted and clarified. For analysis of native biological material, IR spectroscopy is less adequate because the peaks normally will be very broad and overlapping. For such peaks, derivation and deconvolution tend to increase the noise and may give meaningless peaks *[Schultz & Burns 1990]*. However, FTIR has been reported used with success for quantitative analysis of wood. Schultz et al. *[1985]* attained calibrations with high predictive ability for glucose, xylose and lignin content of hardwood samples. Both *[Schultz & Burns 1990]* and *[Schultz et al. 1985]* give literature references to further examples of FTIR used for determination of constituents in wood.

Infrared spectroscopy is a useful laboratory method, but in its present form it has no potential for measuring pulp wood in practice.

In applications for moisture content measurement using thermal conductivity, infrared radiation is used for heating and infrared emission from the specimens is used for sensing temperature changes (see chapter 8).

## 4.8 Microwaves

The microwave wavelength range is between  $10^{-3}$  and  $10^0$  m, i.e.  $10^8$  to  $10^{11}$  Hz. As for electromagnetic waves of other wavelengths, the principle when determining wood properties is to measure how the wood affects the waves and establish connections to the desired wood properties by a calibration model. The measured parameters are either the propagation speed, attenuation or phase shift of the waves or (one of) the dielectrical properties (the dielectric constant and/or the loss tangent). When using microwaves for detection of knots or other areas with irregular grain, a linear polarized wave is used. The depolarization of the wave will then be a measure of the grain direction *[James et al. 1985]*. The waves can be detected and analyzed either when reflected from the wood or when transmitted through it.

According to James et al. [1985] the attenuation of microwaves predominantly is a measure of the water content, while the phase shift reflects both moisture content and density. Both Tiuri et al. [1980] and Kraszewski [1980] discuss the difficulties in measuring the water content of wood using microwaves, when one does not have knowledge of the density. Measuring just one wave parameter will then not be enough because the reading will reflect both moisture content and density. The problem can be solved by either measuring the density by using another technique (for example  $\gamma$ -ray as described by Tiuri [*op. cit.*]) or by measuring another wave parameter in addition (for example the phase shift as described by Kraszewski [*op. cit.*]) and then solve the two resulting equations for the two wood properties (see [Kraszewski *op. cit.*] for details). James et al. [1985] describe measurements with a 4.81 GHz transmission instrument. From analysis of the amplitude and the phase of the transmitted waves it was possible to infer both moisture content (up to above 100 per cent) and density, if the thickness of the sample was known. They experienced some problems with spurious reflection of microwaves from the sample holder.

If one is only interested in the moisture content and not the density, one way to handle the problem of density affecting moisture content measurements seems to be to use longer wave lengths, i.e. radio frequencies. Dennis & Beall [1977] tested a moisture meter working at 7 MHz and found that the density of the specimens did not influence the readings. They did, however, find a dependency of specimen thickness because the instrument was one-sided and was affected only by wood within a certain distance. For stems or boards with normal decreasing moisture gradients from centre to surface, a given instrument reading will accordingly correspond to a higher average moisture content for a thick specimen than for a thin specimen.

What is mentioned in 3.2 about how the dielectric properties are affected by the moisture content and density of wood also applies to the microwave range. Dielectric moisture meters use the differences in either dielectric constant (capacitance meters) or in loss factor (power loss meters). A study by Lowery and Kotok [1967] showed that a relatively high accuracy can be attained when measuring the moisture content of green and dry boards with a capacitance meter, but that the readings are sensitive to the density and the temperature, i.e., these factors are not included in the calibration but must be held at the same level as during calibration. Also Busker [1968] experienced temperature influence on moisture measurements. He ascribed the influence of temperature to changes in hydrogen bonding. Busker [*op. cit.*] apparently succeeded in avoiding problems with sample holders by letting both energy source and detector be separated from the sample by air gaps. Measurements made by Mackay [1976] indicate that power loss meters penetrate less than 5 mm into the wood.

Concerning pulp wood, microwave instruments have the advantage of being able to measure both water content above FSP and density simultaneously. Since water causes considerable attenuation one can anticipate problems, if the surfaces of the samples are wet. I.e., measurements direct on the stems are probably not possible with the present technique.

### 4.8.1 Radar

Blomqvist et. al [1986] tested the radar technique for measuring the dry matter content of sawdust. A 500 MHz radar signal was sent through the sawdust and was reflected from the container bottom. Higher frequencies would give better resolution, but also weaker reflections, since more energy would be absorbed. The wavelength was on average 0.25 m. The speed of propagation was calculated from the path length (the thickness of the sawdust layer, which was around 2.5 m) and the time from the signal was sent until the reflection from the container bottom was received (in the order of ns). For each container, the reference average dry matter content was found from samples. A good linear relationship was found between speed and dry matter content of non-frozen sawdust (based on 26 containers, 3 radar measurements per container), while a small study on partly frozen sawdust gave poor results. Apart from water content, the speed also depends on temperature, density and chemical composition, but the results show that the water content overrules these factors.

The speed of propagation is determined by the water content "per metre", i.e. per volume unit, while the water content of interest (the reference) is measured on a weight basis. Therefore the stability of a calibration depends on a constant interrelation between water content per volume unit and dry matter content per weight unit, i.e. constant packing and constant basic density. Concerning a possible application for pulpwood, this dependency is a drawback of the method. Smaller practical problems are the need of a reflector and of measurement of the path length. Since 1986, no further research has been carried out on the technique [Mats Nylinder, pers. com. 1993].

## 5 Mechanical waves

As for electromagnetic waves, non-destructive testing by use of mechanical waves is based on comparison between the applied waves and characteristics of the waves after interaction with the specimen to be measured. There are four different types of mechanical waves (listed in descending order of velocity):

1. Longitudinal waves (also denoted compression waves) for which the particle movement is parallel to the direction of wave propagation.
2. Transverse waves (also denoted shear waves) for which the particle movement is perpendicular to the direction of propagation.
3. Torsional waves for which each transverse section of the material remains in its original plane and rotates about the axis of propagation.
4. Surface (or Rayleigh) waves, which are a kind of transverse waves confined to the surface layer.

Non-destructive testing methods are classified according to the wavelength applied and how the propagating waves are induced into the wood. This can either be done by mechanical stress or by use of transducers. The three main techniques are acoustic emission (AE), ultrasonics (US) and acousto-ultrasonics (AU). Their main differences and similarities from a flaw detection view point are presented in Table 9.

	Acoustic Emission (AE)	Ultrasonics (US)	Acousto-ultrasonics (AU)
Energy source	Active fracture	External Transducer	
Frequency	30 kHz - 1 MHz	0.5 - 2.0 MHz	100 kHz - 1 MHz
Signals	Not repeatable	Repeatable	
Flaw imaging	Not possible	Macroscopic	Microscopic
Flaw source location	Triangulation	Scanning	Triangulation or scanning
Major Parameter measured	Emission rate and amplitude	Velocity change	Energy dissipation

Table 9. "General comparison of ultrasonics techniques for defect sensing". Table and text from [Beall 1989].

A review of the three techniques mentioned in Table 9 as applied to wood is given by [Beall 1989]. The review includes a glossary and a comprehensive list of references. Adjacent

techniques based on inducing mechanical waves are vibration response and stress wave techniques. In both methods the waves are induced mechanically (for example by use of a hammer). In vibration response, the effect is measured in terms of the resulting vibration of the specimen, while for stress wave techniques the propagating wave is considered.

Regardless of the method, the wave characteristic normally measured is either the attenuation (which expresses the energy dissipation and is frequency dependent) or the propagation speed. For constant spacing of wave inducer and receiver, transit time, also denoted time-of-flight is often used instead of propagation speed. The wave inducer and the receiver can either be placed on opposite sites of the medium, i.e. transmission measurement or on the same side. In the last case two different set-ups are possible, if transducers are used: pulse-echo, in which case one transducer both induces and receives, and pitch-catch, in which one transducer is dedicated at inducing waves, while the other receives. The pulse-echo approach requires a damped transducer that is ready to receive the echo shortly after having induced a wave.

For solid wood, both propagation velocity and attenuation depend on the direction of the wave in relation to the grain. The velocity in the longitudinal direction is approximately three times the velocity in the radial direction, which in turn is almost double the velocity in the tangential direction [Burmester 1967], [Bucur 1983]. Attenuation is between 10 to 30 per cent larger in the tangential and radial directions than in the axial [Burmester *op.cit.*].

The acoustic impedance of a material is defined as the product of the density of the material and the sound velocity in the material. When sound waves propagating in one material hit the boundary to another material, the relationship between the impedance of the two materials will be decisive for how large a part of the wave energy will be reflected from the boundary and how large a part will be transmitted. If the impedance differs greatly between the two materials, essentially all wave energy will be reflected. This is the case between wood and air, while the difference between water and wood is less pronounced [Birch 1990]. When applying sound waves to wood by use of transducers, it is therefore of the outmost importance to prevent that the waves have to travel between air and wood. One way is to secure the contact between transducer and wood by use of a water based high viscosity coupling medium, another to submerge the wood in water. The contact can also be established by using pin like steel waveguides driven into the wood. Generally, coupling between transducers and wood is the main problem when applying ultrasonics to wood, [Beall 1989] and others.

A considerable part of the available publications on the use of mechanical waves for non-destructive evaluation of solid wood or boards concerns measuring the strength of the specimens, i.e. the modulus of elasticity (MOE) or the modulus of rupture (MOR). Examples are [Dunlop 1980], [Waubke & Märkl 1982], [Dean & Kaiserlik 1984], [Greubel & Merkel 1987], [Ross & Pellerin 1988], [Sandoz 1989] and [Arrima *et al.* 1990 and 1991]. Another group of publications concentrates on the use of mechanical waves for detection of decay, see



for example [Waid & Woodman 1957], [Konarski & Ważny 1977] and [Wilcox 1988]. The bulk of the articles mention the effect of moisture content and/or density (normally mass or specific density) en passant or as parameters to be included in the calibration models for strength to reduce the model error. The findings concerning the influence of moisture content or density on the velocity or attenuation of mechanical waves are not completely in agreement as the following list indicates:

[Arima *et al.* 1990]: Effect on frequency of both specific density and moisture content, both below and above FSP (longitudinal vibration response, solid wood).

[Arima *et al.* 1991]: Frequency of longitudinal wave varies with gross density. Moisture effects the response below FSP, no affect above FSP (longitudinal vibration response, solid wood).

[Beall 1989]: Attenuation (US and AU) parallel to grain is inverse proportional to density (kind of density not specified).

[Konarski & Ważny 1977]: Moisture content (below FSP) and gross density effect transit time of ultrasonic waves.

[Pellerin 1965]: Moisture content (below FSP) effects the readings (vibration response).

[Szymani & McDonald 1981]: Ultrasonic waves are not affected by density or moisture content (solid wood).

Three publications concentrating on clarifying which factors effect the propagation of ultrasonic waves through wood are [Burmester 1965 and 1967] and [Lemaster & Quarles 1990]. Burmester [1965] finds that the velocity of ultrasonic waves at 100 KHz decrease linearly with increasing moisture content of wood (Scots pine), both below and above the FSP. The rate of decrease is larger below the FSP. For specific density at 12 per cent moisture content, no clear relationship to ultrasonic velocity was found, i.e. the relationship differs from tree species to tree species (five different species were considered). Lemaster & Quarles [1990] found no systematic effect of density or moisture content on attenuation (AU, solid wood).

In all, vibration response seems to be affected by moisture content (at least below the FSP), while there is no clear pattern for whether and in which way sonic and ultrasonic waves propagating in wood are influenced by moisture and density.

Because the influence of basic density and moisture content on the attenuation and velocity of mechanical waves in wood apparently isn't clarified, no conclusion concerning its possible use for pulp wood can be given. Perhaps the very fact that the relationship isn't clarified yet, even though non-destructive testing of wood by mechanical waves was introduced more than thirty years ago indicates that the relationships are not simple. Whichever the relationship, the literature found indicates that problems with coupling between wood and transducers can be anticipated for methods including transducers. The literature also suggests that relatively low frequencies should be used (i.e. 1-200 kHz, which is low compared to the frequencies normally applied for flaw detection in metals).

## 6 Particle absorption/slowing

This chapter presents evaluation methods based on absorption or slowing of particles sent through the sample. Beta particles and neutrons are used for this purpose, while their limited range have limited the use of alpha particles [Loos 1965]. All applications of beta and neutron rays imply health hazards and environmental risks.

### 6.1 Beta rays

Beta ray transmission was the first radiation technique used for densitometry of wood [Polge 1969]. Beta particles are high energy electrons emitted from certain unstable nuclei [Cameron et al. 1959]. Their range in wood with a specific density around 0.5 is approximately two centimeters [Loos 1965]. Cameron et al. [op.cit.] describe a system using a  $^{90}\text{Sr}$  source in equilibrium with its daughter product  $^{90}\text{Y}$ , while Phillips [1968] uses the weaker emitter  $^{14}\text{C}$  as a source. The technique was introduced for wood by Phillips and co-workers around 1960 [Cameron et al. 1959], [Phillips 1960]. Kleuters [1964] describes how to optimize the method. The beta ray method is very similar to direct scanning X-ray densitometry. Beta rays from the source are collimated and sent through the sample, the transmitted rays are detected and a density profile is recorded. The density profile is then used for detailed analysis of density variation patterns within and between rings. See [Harris & Polge 1967], [Phillips 1968] and [Polge 1969] for a comparison of X-ray photo densitometry and the beta ray technique and discussion of their strong and weak sides. As for X-ray densitometry, it is the specific density that is measured. Similarly, the measurement requires a fixed water content and the thickness of the sample must be known.

Like X-ray densitometry, the beta ray densitometry has no potential for pulpwood scaling.

### 6.2 Neutron rays

Where no other reference is mentioned, the following is based on [Aslyng 1976].

A fast neutron source consists of an alpha emitting radioactive isotope (for example  $^{226}\text{Ra}$  or  $^{241}\text{Am}$ ) in connection with beryllium. One alpha particle reacts with one beryllium atom resulting in one carbon atom and a fast neutron. When a fast neutron collides with an atom, part of its energy is transferred to the atom. After a number of collisions, the energy left for the neutron will be so low, that it now only moves due to diffusion. Such slow neutrons are denoted *thermal* neutrons. Thermal neutrons can be detected using a Geiger-Müller tube or a scintillator. Hydrogen is by far the elemental that most effectively slows down neutrons. If the content of hydrogen is constant in the dry part of a substance, the number of thermal

neutrons detected is therefore proportional to the water content per unit volume, when samples of the substance are radiated with fast neutrons.

According to Szymani and McDonald [1981] applications of moisture content determination using neutron rays exist for soil, food and bulk materials. Gibson & Rusten [1964] describe determination of moisture content (weight water per unit volume) in pulp chips by use of neutron rays. The radioactive source used ( $^{226}\text{Ra}$ ) also emits gamma rays, and gamma ray back scattering is used for obtaining bulk density (weight of wet chips per unit volume wet chips). Moisture content on dry (or wet) weight basis can then be calculated.

For determination of moisture content of pulp wood by use of neutron rays it is a problem that it is the water content per unit volume and not the water content per unit weight that is determined. The approach used by Gibson and Rusten [*op.cit.*] solves this problem.

## 7 Nuclear magnetic resonance (NMR)

Where no other reference is mentioned, the first four paragraphs of this chapter are based on [Fukushima & Roeder 1981].

As the name indicates, nuclear magnetic resonance (NMR) is a technique based on the magnetic spin of nuclei. Normally the nuclei are oriented randomly. But when placed in a magnetic field, the nuclei will align parallel to the field, because this is the position in which they possess less potential energy. If energy is supplied in the form of electromagnetic radiation with the right wavelength, the nuclei will change orientation and will start to precess around an anti parallel direction. The frequency for which a nucleon resonates (i.e. tips to an antiparallel direction) is unique for each combination of field strength and isotope, and is denoted the Larmor frequency  $\nu_L$ . The Larmor frequency is related to the strength of the magnetic field  $H_0$  by the Larmor equation:  $\nu_L = \gamma H_0$ , where  $\gamma$  is a parameter denoted the gyromagnetic ratio. For the field strengths normally applied, the Larmor frequency belongs in the radio frequency range. When nuclei have absorbed radiation, they will emit radiation at the same wavelength and change back to the lowest energy state. Thus the Larmor frequency is

characterized by both strong absorption and strong emission of radiation. The nucleon used most abundantly in NMR is  $^1\text{H}$ , the proton. Proton-based NMR is sometimes denoted HTNMR for hydrogen transient NMR [Svensson *et al.* 1992]. Two types of NMR dominate in the papers describing use of NMR for wood: steady-state (also denoted continuous or wide line) NMR and pulse NMR.

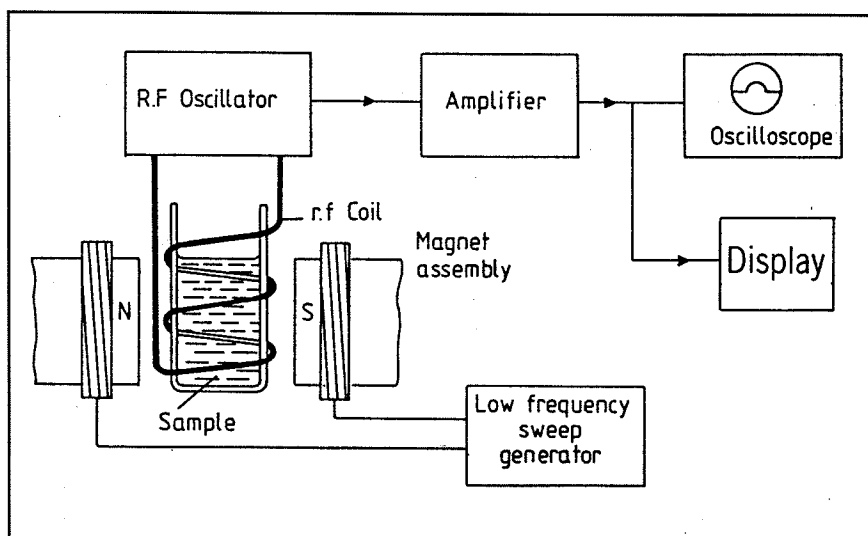


Figure 7. "Basic arrangement of continuous NMR". Figure and text from [Young 1989].

The basic arrangement of continuous NMR is shown in Figure 7. The sample is subject to both an alternating RF field at a constant frequency and a strong homogeneous magnetic field. The strength of the applied magnetic field is varied. The nuclei will absorb and emit when the Larmor equation is fulfilled. In this way a spectrum of energy absorbed versus magnetic field strength is obtained. A measure of the energy absorbed is obtained from the voltage induced in the coil, the coil works both as transmitter and receiver of RF radiation. The resulting spectrum normally has the form of "concentric" Gauss or Lorentzian curves, i.e.

centered on the same field strength, but with different amplitude and width. Generally, water-hydrogen produces a high, narrow peak, while hydrogen build-in in the solid part of a sample produces a low, broad peak.

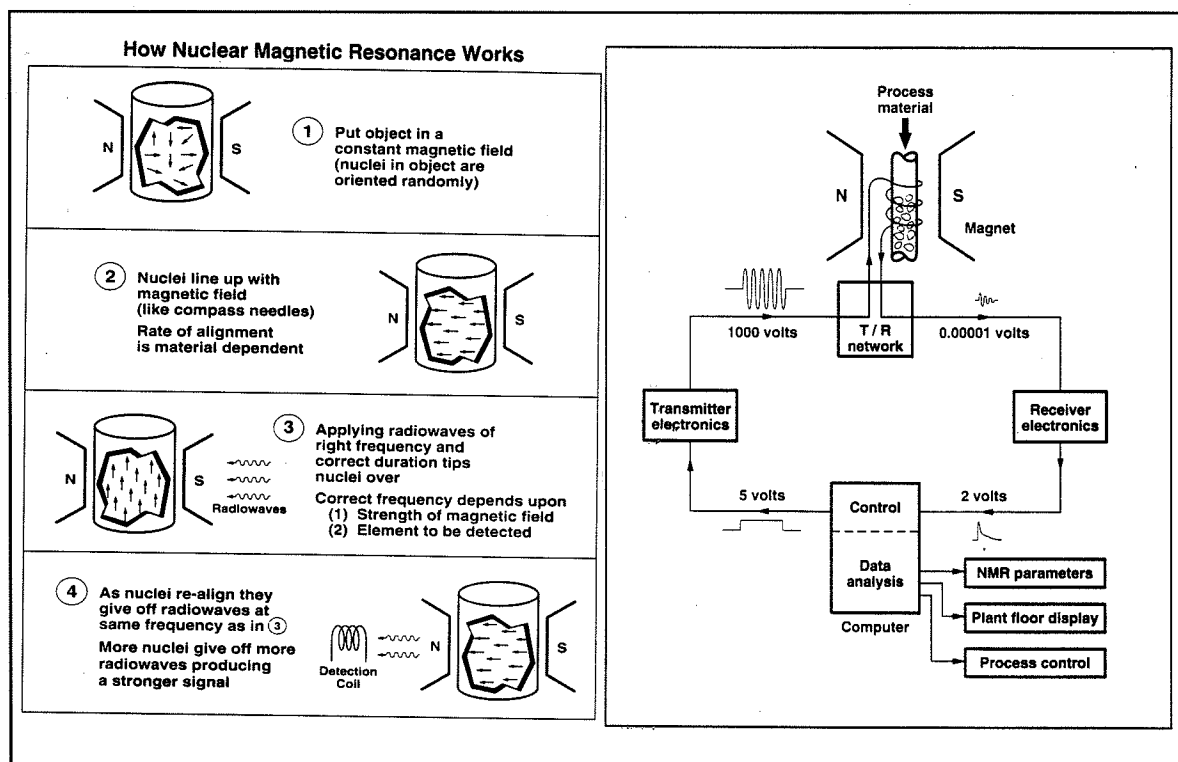


Figure 8. Pulsed NMR. From [Nicholls 1991].

The basic principle of pulse NMR is shown in the left part of Figure 8, while a diagram of the setup is shown to the right. When first placed in the homogeneous magnetic field, the nuclei of the sample will begin to align parallel to the field. The time constant characterizing the rate at which this happens is called the longitudinal or the spin-lattice relaxation time,  $T_1$ . After the  $90^\circ$  pulse, the amplitude of the sinusoidal alternating electricity induced in the receiver coil will decay exponentially with a time constant called the transverse or spin-spin relaxation time,  $T_2^*$ . The signal induced in the coil as a function of elapsed time since the pulse is called free induction decay (FID). The resulting curve is called a FID curve or an interferogram. The amplitude of the signal is a measure of the number of (hydrogen) nuclei present in the sample. A FID for moist wood will consist of a rapidly decaying signal from the solid wood and a slowly decaying signal originating from the "free" water. The relaxation times are measures of the rate of redistribution of energy following excitation of the nuclei.  $T_1$  to the lattice, i.e., energy forms other than spinning in the rest of the sample, for example vibration,  $T_2^*$  to magnetic spin of the surrounding nuclei. Both  $T_1$  and  $T_2^*$  depend on the nuclei present and their binding states. For solids,  $T_1$  is much larger than  $T_2^*$ , while for

liquids they are of the same size.  $T_2^*$  depends on both  $T_1$  and  $T_2'$ , which results from dipolar processes:

$$\frac{1}{T_2^*} \approx \frac{1}{2T_1} + \frac{1}{T_2'} + \gamma\Delta H_0$$

where  $\Delta H_0$  is the inhomogeneity of the applied magnetic field.  $T_1$  dominates for liquids, while  $T_2'$  dominates for solids. Because of inhomogeneity of the applied magnetic field, which is due to magnet imperfections, all parts of the sample will not experience the same magnetic field strength. Small volumes of the sample to which the same field strength is applied are called spin isochromates. Each spin isochromate has its own intrinsic transverse relaxation time, denoted  $T_2$ .  $T_2^*$  and  $T_2$  are related by

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta H_0$$

Thus, the more homogeneous the magnetic field, the smaller and more identical with  $T_2$  will  $T_2^*$  be. One effect of the magnet imperfections is that when recording FID's for moist samples, the signals will be similar for samples holding more than a certain amount of water [Svensson *et al.* 1992]. There is a way to overcome the problem of magnet imperfections, and that is to use a sequence (or train) of pulses and echoes. The Carr-Purcell echo train [Carr & Purcell 1954] uses a  $90^\circ$  pulse followed by  $180^\circ$  pulses. This normally leads to an error accumulation resulting in too short  $T_2$  being measured. The Meiboom-Gill modification [Meiboom & Gill 1958] of the Carr-Purcell sequence (denoted CPMG) avoids this problem by applying pulses that are phase shifted  $90^\circ$  with respect to the initial  $90^\circ$  pulse. The curve through the amplitude maxima of the signals equals a normal FID, and can be used for deriving  $T_2$ .

Other types of NMR are FT-NMR, CP NMR and MAS NMR. In Fourier transform NMR, Fourier transforms are used for resolving the FID curve into signals originating from different types of nuclei or nuclei in different environments (i.e. with different bonding, neighbour nuclei or at different temperatures). CP and MAS NMR or cross polarization and magic angle spinning NMR are kinds of NMR dealing with the dipolar interaction between nuclei in solids. In CP NMR, the dipolar interaction between nuclei of one kind is used for enhancing the FID from another kind of nuclei in the sample. In MAS NMR the dipolar interactions are neutralized by spinning the sample at a certain angle ( $54.74^\circ$ ) relative to the magnetic field. CP and MAS NMR can be combined.

NMR can also be used for tomography. This is called magnetic resonance imaging (MRI). According to [Svensson *et al.* 1992], the principle is to apply a magnetic field gradient in such a way that the field strength will vary linearly along the sample in the direction of the gradient (for example along the length of the sample). According to the Larmor equation, the nuclei ( $^1\text{H}$ ) will then resonate at different frequencies dependent upon their position in the field. From the return signal cross sectional views of the sample along the gradient can be constructed. The image construction requires a vast amount of complicated calculations.  $^1\text{H}$

based MRI for wood is explored by Hall & Rajanayagam [1986], Wang & Chang [1986], Wang et al. [1987] and by Olson et al. [1990]. Two-dimensional imaging is used by Quick et al. [1990] and by Araujo et al. [1992]. The structure seen in the images in these papers is the water distribution.

Use of NMR for moisture measurements in wood have followed three lines.

The earliest experimenters used steady state NMR for measuring bulk water content. Examples are [Nanassy 1973, 1974, 1976], [Karras & Rahkamaa 1971] (for pulp) and [Magnusson et al. 1972] (wood and pulp). In his articles Nanassy split each spectrum in a narrow peak and a broad peak. The narrow peak was ascribed to mobile or free water, the broad peak to dry wood and tightly bound water. Below the FSP, Nanassy found an approximate linear relationship between moisture content (dry basis) and the area under the broad peak relative to the area under the broad peak for the same sample prior to remoistening. Using the narrow peak, Karras and Rahkamaa [*op.cit.*] calculated both the area under the curve and the peak height and plotted this against the moisture content. Sigmoid curves were obtained for moisture contents below 10 per cent. Magnusson et al. [*op cit.*] obtained linear relationships between moisture content up to 50 per cent (wet basis) and the area under the curve relative to the sample weight.

Another approach for measuring moisture content in wood by use of NMR implies pulse NMR. Sharp et al. [1978] found a linear relationship between the amplitude of the FID curve at a certain time after the pulse (50  $\mu$ s) and the moisture content, also above the FSP. Svensson et al. [1992] use the CPMG spin-echo train. The first (or second) peak in the train is ascribed to dry matter, while a latter peak is ascribed to water. The relative amplitude of these two peaks shows a linear relationship to wet-based moisture content, also above FSP (if dry-based moisture content is used, the curve will be slightly convex).

A third line of development use NMR as a tool for studying forms of water in wood, i.e. its binding states. Different  $T_2$ 's are extracted from the FID curve, and each of these relaxation times is ascribed to a certain water environment, characterised by a certain binding state of the water. Papers on this and related approaches include [Hsi et al. 1977], [Riggin et al. 1979], [Peemoeller et al 1985], [Menon et al. 1987], [Flibotte 1990], [Hartley et al. 1992] and [Araujo et al. 1994].

As the binding state affects the relaxation times of nuclei, one would expect NMR moisture measurements of wood to be sensitive to temperature, and especially expect a difference between water and ice. According to [Abragam 1961], the start amplitude of the FID curve resulting from a pulse NMR measurement is inversely proportional to the absolute temperature. Using steady state NMR for moisture measurements of solid wood, Nanassy [1978] found no effect on the area under the absorption curve for temperature changes between -30 and 100 °C. Below -30 °C the area decreased with decreasing temperature. For moisture measurements in coal by pulse NMR, Unsworth et al. [1988] found an effect of

temperature on transverse relaxation times, the  $T_2$  increasing with a factor 100 from about - 80 °C to about 0 °C. They found a marked shift at approximately - 80 °C, but unexpectedly none at 0 °C. From this it seems like temperature have only little or no effect on steady state NMR measurements, while a temperature dependency probably will be encountered for pulse NMR measurements of moisture in wood for temperatures normally encountered for nordic pulp wood.

A concise review of studies of the use of NMR for moisture measurements in wood is given in [Hartley et al. 1992].

Pulsed HTNMR might have a potential for measuring dry matter content of pulp wood. It is a very selective method. The moisture content measurement is not dependent on the distribution of the moisture in the bulk volume measured, and is not disturbed by the sample surface. Furthermore it seems to be unaffected by whether the water is frozen or not, at least for temperatures only moderately below the freezing point. However, an effect of temperature on transverse relaxations times may exist. According to Colin Nicholls [Pers. com. 1992], one-sided instruments are possible to construct, but unless very powerful magnets are used, the measured volume will not exceed a few cubic centimeters. NMR is p.t. considered a non-hazardous method, but strong magnetic fields are presently under suspicion for having carcinogenic effects.

According to Nicholls [1991] NMR implementation always needs some customization, which keeps prices up. According to Svensson et al. [1992], prices for a HTNMR sensor system start at approximately \$ 50,000.

I have found no publications commenting on a possible relationship between a NMR - signal and basic density of wood.



## 8 Thermal conductivity

The thermal conductivity (unit:  $\text{W m}^{-1}\text{K}^{-1}$ ) of a substance depends mainly on its elemental composition and bulk density. A priori, there is therefore reason to believe that thermal conductivity of wood would be affected by both moisture content and (basic) density.

Kotok et al. [1969] measured the surface temperature of boards during drying and found that the temperature could be used as an indicator of moisture content. Troughton & Clarke [1987] describe a system for measuring moisture content of veneer and lumber prior to drying. The system is based on heating the wood by infrared heaters and measuring the surface temperature rise by use of infrared heat sensors. Both below and above FSP, the temperature rise, which is measured after a few seconds is mainly a function of the moisture content. Good correlations between surface temperature rise and moisture content were found.

Madsen et. al. [1988] tested thermal conduction as a means to estimate the bio degradation of solid wood. They found a difference in thermal conductivity between fresh and severely degraded wood if the temperature change was measured sufficiently close to the infrared heat source (i.e. closer than 10 mm). The moisture content of the tested wood is not given, but it seems to have been below FSP. However, practical experiments aimed at quantitatively acquiring the specific density at 12.5 and 4.9 per cent moisture content gave poor results. Madsen et. al. [op.cit.] mention insufficient and unstable contact between heat source and wood as a probable reason why only a rough qualitative measurement was possible.

For pulp wood, thermal conductivity could probably be a viable principle for measuring moisture content. For basic density, thermal conductivity probably lacks potential. Measurements of moisture content seems to be unaffected by density. The above mentioned initial test carried out below FSP gave low correlation between specific density and thermal conductivity. Therefore there is reason to expect low correlation also between basic density and thermal conductivity measured above FSP. Further, as only one response variable is recorded, the method is only able of measuring one characteristic (see section 2.1).

## 9 Energy absorption and drilling resistance

If the damage on the specimen caused by a measurement does not influence the planned or continued use of the specimen, the method is in some contexts denoted a nondestructive or quasi-nondestructive method. Concerning pulp wood, energy absorption and drilling resistance belong in this category.

### 9.1 Energy absorption

The principle in energy absorption methods is to fire a pin into the specimen with exact amount of energy and measure the penetration. The penetration will mainly depend on the density and moisture content of the penetrated wood. Other factors influencing the penetration include temperature, tree species, ring width, cell length and preservatives [Abbot & Elcock 1989]. The most widespread instrument working according to the energy absorption principle is the Pilodyn. This instrument exists in several editions varying in energy level (6, 12 and 18 J), with different pin diameters (2-5 mm), tip finish (blunt or pointed) and with or without mechanism for repeated firing [Kalhauge 1988]. The penetration for a non-repeating instrument normally is between 20 and 40 mm.

Concerning moisture content of soft wood (Douglas fir), Smith & Morrell [1986] found a linear relationship between Pilodyn pin penetration and moisture content below FSP, while penetration was unaffected by moisture content changes above FSP. Also Hoffmeyer [1978] saw an influence of moisture content on penetration (for soft wood).

For density, Hoffmeyer [1978] found that Pilodyn penetration perpendicular to annual rings could explain about 80% of the variation in dry density of boards (both soft wood and hard wood) conditioned to 18-24 per cent moisture content. Cown [1982] found a significant relationship between Pilodyn penetration and mean basic density of groups of standing trees. The bark was removed before the pin was shot into the trees, and one measurement was done per tree. [Taylor 1981] found a good correlation between Pilodyn penetration and specific density.

Concerning pulp wood, energy absorption could be an alternative for classification into basic density classes - as long as the wood is not frozen. For measuring moisture content of pulp wood, the principle has no potential.

### 9.2 Drilling resistance

Drilling resistance instruments drill a hole in the wood to be tested. The tip of the boring needle is normally 1-3 mm in diameter and the needle is normally 300-500 mm in length. The tip of the needle must be wider than the rest of the needle to secure that the resistance originates from the tip and not from the shaft. Drilling resistance instruments can work

according to one of two principles. Either the propagation speed of the needle is held constant and the current consumption is recorded or the current consumption is constant and the propagation speed is recorded. Typical speeds are 70-280 mm/min [Anonymous 1993b]. In both cases the result is a profile reflecting drilling resistance along the path of the needle tip. Drilling resistance instruments can be used for in situ detection of decay and insect damages in built-in timber and standing trees [Anonymous 1993b]. Some instruments can give more detailed density profiles for tree ring analysis (i.e. a counterpart to X-ray densitometry). Görlacher [1991] used an instrument of the constant speed type for measuring average density of small wood specimens (species not given). The mean effective drilling resistance was calculated for each specimen by dividing the area under the drilling resistance curve by the drilling distance. A good correlation to specific density at 12 per cent moisture content was found. Görlacher [*op.cit.*] assumes that also the moisture content affects the drilling resistance.

Concerning pulp wood, drilling resistance instruments might have a potential for density estimation using the above described Görlacher approach. But it requires that a possible influence of moisture content is clarified, and that the boring speed is raised. Single measurement times of approximately  $\frac{1}{2}$  to 1 minute are probably too long for real time applications. For frozen wood, the method might prove less adequate.

## 10 Conclusion

Table 10 sums up the conclusions from the previous chapters concerning the applicability of the presented measuring principles for pulp wood scaling. The evaluations are subjective and may hold errors both due to lack of information and misjudgements. The abbreviations used in the table are explained on the next page.

Principle		Potential for measuring			MC meas. dep. on BD?	BD meas. dep. on MC?	s/l/v	Pot. for pulp wood?
		MC<FSP	MC>FSP	BD				
Electricity	Resistance	yes	no	no	yes	-	l	no
	Dielectric properties	yes	yes	yes	yes	yes	l	yes
	Eddy current	?	?	?	?	?	v	?
	Piezoelectric effect	no (only 0-20 %)	no	?	yes	yes	v	no
Electromagnetic waves	Gamma rays	yes	yes	yes	yes	yes	l	yes
	X-rays <sup>3</sup>	yes	yes	no	no	-	l	maybe
	Fluorescence spectroscopy	?	?	?	?	?	s	no
	Near infrared spectroscopy	yes	yes	yes?	no	no	s/v	yes
	Infrared spectroscopy	no?	no?	no?	?	?	s/v	no
	Microwaves	yes	yes	yes	yes	yes	s/l	yes
Mechanical waves	Radiowaves	yes	yes	no	no	-	v	yes
	Acoustic emission	no	no	no	-	-	-	no
	Ultrasonics	?	?	?	?	?	v	no?
	Acousto-ultrasonics	?	?	?	?	?	v	no?
	Vibration response	yes	?	yes	yes?	yes?	v	no
	Stress wave	?	?	?	?	?	v	no
NMR		yes	yes	?	no	?	v	yes
Particle absorption/slowing	Beta rays	no	no	no	-	-	l	no
	Neutron rays	yes	yes	no	yes	-	v	maybe
Thermal conductivity		yes	yes	no	no	-	v	yes
Energy absorption and drilling resistance	Energy absorption	no	no	yes?	-	no	l	maybe
	Drilling resistance	no?	no?	yes	-	no?	l	maybe

Table 10. Overview over the applicability for pulp wood of the measuring methods reviewed in this report.

## Abbreviations used in Table 10:

MC	moisture content
FSP	fiber saturation point
BD	basic density
meas.	measurement
dep.	dependent
s/l/v	indicates whether measurement takes place on the surface of the sample, along a line through the sample or covers a part of the sample volume.

The table indicates that NIR is the single most promising principle. Also NMR and microwaves are promising techniques.

In this report, the potential of each of the various methods is evaluated separately. However, in other parts of the wood working industries, one of the trends concerning NDE is the use of combinations of principles rather than just one. For example simultaneous use of gamma rays for density measurement and microwaves for moisture content determination. Similar combinations could also be applied to pulp wood.

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## Appendix A

### Multivariate calibration in NIR

It is outside the scope of this report to give a covering description of multivariate calibration, especially as various textbooks and tutorials exist on the subject. This appendix only gives an introduction to analyzing techniques for multivariate calibration in near infrared spectroscopy (NIR). An introduction to calibration and indirect measuring is given in section 2.1. This appendix first gives an overview over the subject, then the various subjects are treated in more detail.

As described in section 4.6, there are two types of NIR instruments: those measuring at a few wavelengths (1-20) and those recording a whole scan (several hundred wavelengths). Calibration of instruments belonging in the first category is normally done by multiple linear regression (MLR), because the MLR presumption that the variables are independent of each other holds for these instruments. Normal MLR calibration will not be described in this appendix. For the other class the response signals from neighbouring wavelengths are normally highly correlated, which makes MLR impossible. For these instruments the normal procedure is to calibrate in two steps: first a data compression is carried out, which removes redundant information, then a calibration model is produced linking the compressed data to the response variable(s). For some calibration methods these two steps are tied together. In some cases a mathematic preprocessing of the spectra before the compression can improve the calibration model. The response variable(s) can either be qualitative or quantitative. In the qualitative case the purpose of the calibration is to teach the instrument to assign an unknown sample to one of a number of sample classes (or to none of them, if the sample deviates from all the types the instrument knows). In the quantitative case, the purpose is to teach the instrument to give an estimate of the value(s) of the response variable(s). In some NIR applications qualitative analysis is followed by quantitative: first a qualitative analysis is applied to ascribe the sample to one of a number of classes, then the value of the response variable(s) is predicted according to a quantitative calibration model fitted to that class. The benchmark for the quality of a calibration model is its predictive ability for unknown samples. The ability of the calibration system to detect outliers (during calibration as well as when predicting for unknown samples) is also important.

All aspects of quantitative multivariate calibration are treated thoroughly by Martens and Næs [1989]. An overview over qualitative analysis using NIR is given by Mark [1992b].

#### Preprocessing

Mathematic preprocessing of near infrared spectra prior to the calibration can sometimes give calibration models with better predictive ability and/or a more simple composition. On the other hand, any preprocessing implies a risk of losing information that might have been useful in the calibration and of magnifying irrelevant noise. Therefore no preprocessing should be applied without thorough consideration of its relevance and of its consequences. Below, an overview is given over commonly used preprocessing.

*Preprocessing aimed at linearizing the response signal*

Transformation to absorbance Relative (or absolute) reflectance and transmittance can be transformed to absorbance  $A$  by the formula  $A = \log(I/X)$  where  $X$  is either reflectance or transmittance. This formula originates from Beer-Lambert's law, i.e.  $I = I_0 e^{-\mu x}$ , where  $I$  is the intensity of radiation after passage of substance of the thickness  $x$  and with the absorptivity  $\mu$ , when the start intensity of the radiation is  $I_0$ . The formula can be transformed to  $\log(I_0/I) = A$ , where  $A$  is equal to  $\mu x$  ( $\mu$  adjusted to logarithmic base 10).  $A$  is sometimes denoted *Optical Density* (O.D.), and is given in *O.D.-units*. Transmittance is defined as  $I/I_0$ , hence the above formula when  $X$  is transmittance. When the formula is used also for reflectance, it is based on the assumption that reflectance and transmittance hold the same information of the object. Thus, the transformation is only loosely founded for reflectance. Further, the above formulas presupposes that transmittance is measured absolute, not relative. Perhaps one should therefore instead think of the transformation only as a remedy, which can sometimes linearize the relationship between the response signal and the response variable.

Kubelka-Munk Kubelka & Munk [1932] gave a formula for the relationship between the reflectance  $R$  and the concentration  $c$  of an absorbing analyte with the absorptivity  $\mu$ :

$$\frac{(1-R)^2}{2R} = \frac{(\ln 10)\mu c}{S}$$

where  $S$  is a constant known as the scattering coefficient.

In arriving at this equation, Kubelka and Munk made several assumptions concerning the sample texture and the radiation flux. The left side of the equation is known as the *Kubelka-Munk function*, and is usually denoted  $f(R)$ . It is this function that is used for transformation of reflectance spectra. As can be seen, the equation indicates a linear relationship between  $f(R)$  and  $c$ . According to Olinger & Griffiths [1992] this will not hold if the analyte is surrounded by an absorbing matrix or if the absorption bands are strong (fundamentals and/or high analyte concentration).

*Preprocessing aimed at giving all variables equal chance for influencing the model*

Standardization (also called autoscaling) is to multiply for each object the value of each variable with  $1/\text{standard deviation}$  for that variable. If the values of all variables have approximately the same range (as in spectroscopy), standardization is normally not necessary. If the values of the various variables differ with orders of magnitude, standardization will normally greatly improve the calibration model. One should, however, keep in mind that standardization will magnify the importance of variables that differ only a little in value between objects and minify the importance of variables that differ much in value between objects, regardless of how relevant the variables are for the response variable. If standardization is carried out, one should therefore carefully consider the resulting weights of the variables in the light of ones a priori knowledge of the measuring technique and situation, and decide whether the weighing makes sense.

Logarithmic transformation of an independent or response variable can give a better ground for the modelling in the case where a few objects have very high values for that variable, while the rest have very low. If logarithmic transformation is not carried out, the few objects will occupy almost all variation in the variable, whereby the possibly useful information laying in the differences between the rest of the objects will be suppressed.

PCA of groups of variables PCA is described in the section on qualitative analysis. PCA of groups of variables is a way to handle the case where one wants to give groups of variables equal chance rather than each variable. An example: both a 500 datapoints spectrum and the temperature is measured for each object. Based on knowledge about the system it is decided to give the temperature higher weight than the default 1/501. One way to do this is to replace the spectra with their scores for the first principal components, increasing the relative importance of the temperature to for example 1/5, if the first four components are used.

*Preprocessing aimed at separating relevant information from noise or irrelevant information*  
Smoothing The purpose of smoothing is to remove from the spectra high frequency noise manifested as sawtooths. According to McClure [1992] the three most popular methods for smoothing spectra are 1) Moving point average (MPA) 2) Polynomial and 3) Fourier.

MPA implies replacing each data point in the spectrum with the average of the point and of a number of neighbour points on both sides. The higher the number, the more severe is the smoothing. A number of points (dependent on the number of points used in the averaging) are lost in both ends of the spectrum.

In polynomial smoothing a polynomial is first fitted by least-squares techniques to a number of sequential data points around the point in question. The value for this centre point is afterwards computed from the resulting polynomial. Also in this case points are lost in both ends of the spectrum.

In Fourier regression, each spectrum is approximated by a sum of cosine and/or sine functions. By including many functions a spectrum can be approximated very closely, but by omitting some of the functions, the spectrum will instead be smoothed. When formulated as a Fourier regression, a spectrum can more easily be subject to various mathematical treatments (see e.g. [McClure 1992] and [Dam 1988]).

Derivation is useful for removing baseline shifts between objects and baseline slopes at the same time as it emphasizes changes of slope. In spectroscopy, derivation means replacement of each data point in the spectra by the slope of an adjacent secant. The secant can for example be the one from the datapoint in question to the next datapoint, the one from the previous data point to the datapoint in question or the one from the previous point to the next data point. Broader gaps between end points of the secants can also be used. One or more points are lost in one or both ends of the spectrum (unless the derivation is calculated by Fourier transformation as described by McClure [1992]). Which ever the case, what is computed is

actually a difference spectrum but it is normally denoted a derivation spectrum. Second derivatives may sometimes give more informative spectra than raw spectra or first derivatives, especially if the purpose is detailed study of weak absorption bands. For noisy spectra derivation is normally followed by MPA (described above), because derivation magnify sawtooth-like noise.

Normalization The purpose of normalization is to transform the data to approximately the same scaling, thereby reducing baseline shifts between objects. For every object normalization can for example be done by replacing each datapoint by the ratio between the reflectance (absorption) at that wavelength and the average reflectance (absorption) for the spectrum for that object. However, the word "normalization" is ambiguous, and if the software one uses offers "normalization", one should check what is meant by this word for this particular program, before applying.

Multiplicative Signal Correction (MSC) is a method aimed at separating relevant information from additive and multiplicative noise. It was developed for removing scatter effects from near infrared reflectance spectra, and was originally called multiplicative scatter correction. The method is described by Geladi et al. [1985] and by Isaksson & Næs [1988]. In the form normally applied to NIR, an average spectrum  $X_{avg}$  is calculated, and each spectrum  $X$  is regressed on this spectrum:  $X = a + b X_{avg} + E$ , where  $a$  and  $b$  are the regression coefficients.  $E$  is the unexplained part of the spectrum, ideally the relevant information to be used in the following multivariate calibration. Each corrected spectrum  $X_i$  is afterwards calculated by  $X_i = (X - a)/b$ . MSC has been further developed to PMSC (Piece-wise MSC). In PMSC the regression coefficients are calculated for each data point of each spectrum rather than for each spectrum. The regression coefficients are based on the average spectrum of the surrounding wavelengths. PMSC is described by Isaksson & Kowalski [1993]. Another version of MSC is EMSC (Extended MSC). In EMSC an extra term aimed at compensating for known chemical variabilities is included when estimating  $a$  and  $b$ . EMSC is described by Martens & Stark [1991].

Spectral interference subtraction (SIS) consists of subtracting the spectra of known interferants. The assumption is that the spectrum for a sample is the sum of the spectra of the sample constituents, and that subtraction of the spectra of known interferant constituents leads to more simple and interpretable models with better predictive ability. SIS is described by Martens & Stark [1991].

Table 11 gives examples of the effect of some of the types of preprocessing mentioned above. The data is near infrared reflectance spectra for wood shavings. The models are PCR models (described in the section on quantitative analysis) for basic density. The models are based on a calibration set with 56 objects and are tested on a test set with 14 objects. The table gives the number of components corresponding to the first local minimum in  $RMSEP$  and the  $RMSEP$  for this number of components ( $RMSEP$  is explained in the section on model quality assessment). The table shows that transformation to absorbance or Kubelka-Munk units improves the predictive ability of the model slightly while retaining the optimum number of factors. Derivation, normalization or MSC reduces the prediction error with more than 25 percent, but at the cost of more complicated models (nine factors instead of four).



Preprocessing	No. of factors	RMSEP (in kg m <sup>-3</sup> )
None	4	19.1
Transformation to absorbance	4	18.1
Kubelka-Munk	4	17.0
Derivation	9	14.4
Normalization	9	13.4
MSC	9	14.3

Table 11. Example of the effect of five different types of preprocessing.

### Qualitative analysis

Qualitative analysis is to ascribe unknown samples to one or none of a number of predefined classes. NIR qualitative analysis can be based on a few wavelengths or on whole spectra. Qualitative analysis requires that the response is distinctly different between classes. In the one wavelength case, the classes must differ in level of the measured response (reflectance, transmittance or absorbance). In the spectra case, the shape or the level of the spectra should differ between classes. For manual sorting of samples, it is in many cases sufficient to look at the response signal and compare with the typical response signals of the classes. But if one wants to automate the sorting, for example in an on-line sorting of objects based on NIR spectra, a quantification of the qualitative differences in response (i.e. shape/level of the spectra) is necessary. Limits for the response level for the various classes must also be defined. One way to accomplish this is by use of Principal Component Analysis (PCA) and Mahalanobis distances. Among others, Martens and Næs [1989], Wold et al. [1987] and Mark [1992a] describe PCA. Mahalanobis distances were first described by Mahalanobis [1936]. A short description is given by Weisberg [1980]. Mark [1992b] gives an overview over qualitative analysis in NIR.

#### Principal Component Analysis (PCA)

PCA is a technique for analyzing variance structures in multivariate, possibly collinear data sets. Automatization of qualitative analysis based on spectra is only one of its many possible applications.

In PCA, the  $N \times K$   $X$  matrix consisting of the measured values of  $K$  variables for  $N$  objects is first centered. That is, for each variable, i.e. column in the matrix, the mean value is subtracted from each element in that column. In spectroscopy, the variables represent wavelengths and the objects correspond to samples (or spectra, if the matrix holds more than one spectrum per sample). Then the  $X$  matrix is transformed according to:

$$\mathbf{X}_0 = \mathbf{T} \cdot \mathbf{P}^T + \mathbf{E}$$

Where  $\mathbf{X}_0$  is the centered  $\mathbf{X}$  matrix, dimensions  $N \times K$ ,  
 $\mathbf{T}$  is a  $N \times A$  matrix holding the  $A$  score vectors  $t_a$ ,  
 $\mathbf{P}$  is a  $K \times A$  matrix holding the  $A$  loading vectors  $p_a$  and where  
 $\mathbf{E}$  is a  $N \times K$  matrix holding the residuals.

The meaning of the equation is considered below:

Geometrically one can think of the process like this: all  $N$  spectra are plotted in a  $K$  dimensional space, where each axis corresponds to one variable (wavelength). In this space each spectrum is represented by a point. The first principal component (also denoted factor or loading vector) is then one of the two opposite unit vectors that gives the direction in the point cloud in which the point cloud vary the most. The second principal component is the unit vector that gives the direction with the second highest variation in the point cloud under the restrain that the principal components should be orthogonal to each other. If this process is continued until  $K$  (or  $N$ , whichever is less) principal components are calculated, the space spanned by the principal components describes the point cloud as precisely as the original  $K$  dimensional space, i.e., the operation equals a change to another system of coordinates. If fewer principal components are subtracted, the space spanned by the principal components will not hold all information on the position of the points. The distances between the points and their projections on the principal component hyper plane are called residuals.

An example: If  $N \geq K$  and  $K = 3$ , the maximum number of principal components is three. If  $A = 2$ , the residuals will be the distance between the points and their projection on the plane spanned by the first two principal components. If  $A = 1$ , the residuals will be the distance between the points and their projections on the line defined by the first principal component.

As the loading vectors are unit vectors, their coordinates can be interpreted as the cosine to the angles between the principal components and the axes in the  $K$  dimensional space, and therefore all loadings are between -1 and 1, if they are not scaled. Each of the  $A$  loading vectors has as many coordinates (loadings) as variables (wavelengths). Loadings can among other things be used for analyzing which variables influence or dominate which principal components (numerically high loadings correspond to high influence).

The score vectors hold the coordinates (scores) of the projections of the points onto the  $A$  dimensional hyper plane spanned by the principal components. Each score vector has one score per object (sample or spectrum) and there is as many score vectors as principal components. If no scaling is carried out, all scores are numerically less than the numerically greatest number in the  $\mathbf{X}$  matrix (or rarely equal to). Scores can among other things be used for analyzing which objects influence or dominate which principal components (numerically high coordinates correspond to high influence).

The terminology presented above is not the only one in use. Different textbooks and articles in the field use different versions of the scores/loadings concept. Also, the words *scores* and *loadings* are sometimes used as short notions for what is above called *score vectors* and *loading vectors*.

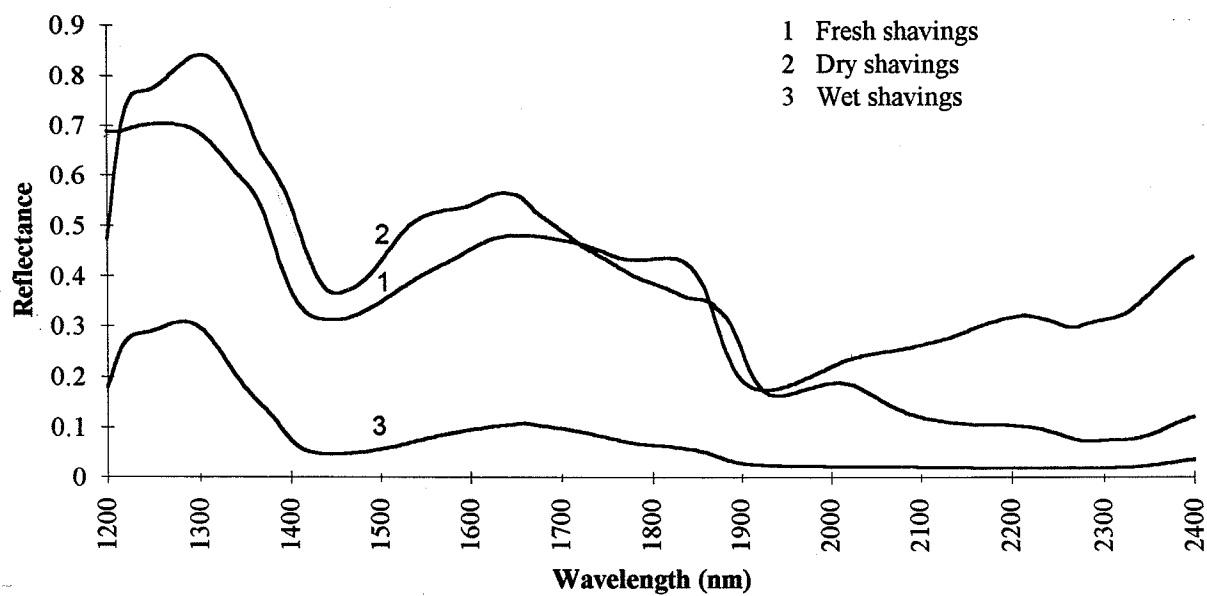
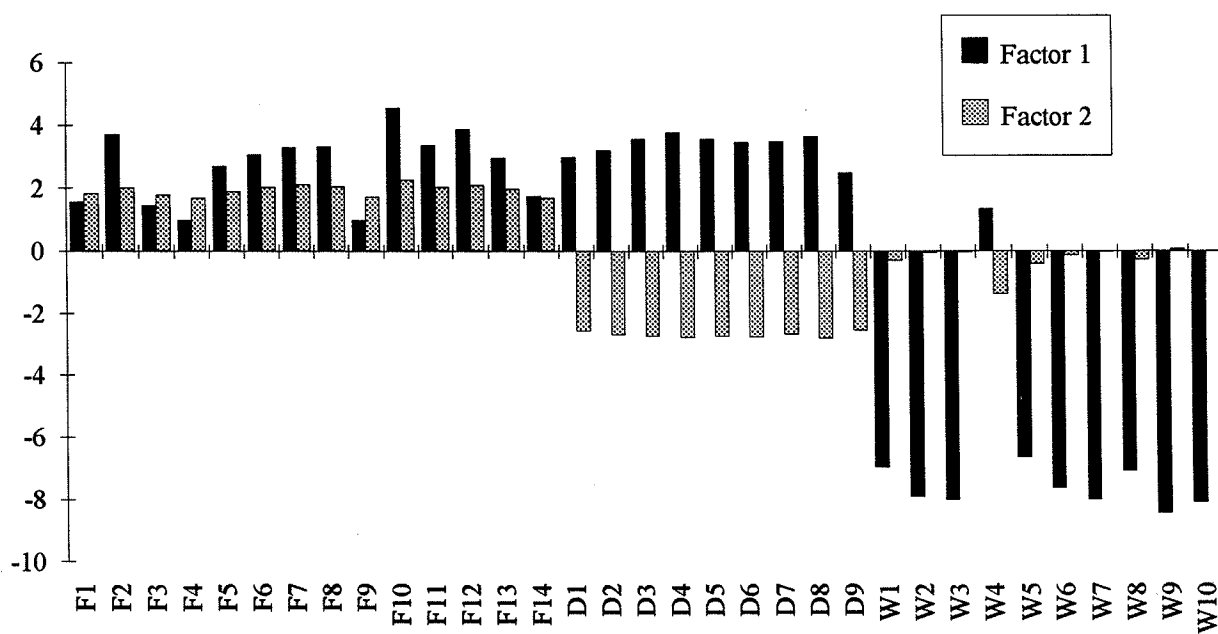
In the mathematic description of PCA, the loading vectors are eigenvectors of the cross-product matrix  $\mathbf{X}_0^T \mathbf{X}_0$ . The score vectors are eigenvectors of the  $\mathbf{X}_0 \mathbf{X}_0^T$  matrix, scaled to lengths equal to the square root of the eigenvalues of  $\mathbf{X}_0^T \mathbf{X}_0$ . This implies that the eigenvalue corresponding to each score vector can be calculated as  $t_a^T t_a$ , i.e., there is a positive relationship between the eigenvalues and the lengths of the score vectors. Thus the eigenvalues (which are in this context always positive or zero) will descend from the first to the last principal component. The higher the eigenvalue, the longer the score vector and the more variability in the data is explained by that principal component. Both score and loading vectors are orthogonal, i.e.,  $t_i^T t_j = 0$  and  $p_i^T p_j = 0$  for  $i \neq j$ .

The algorithm normally used in NIR for decomposition of data to principal components is the NIPALS algorithm, which was first described by Wold [1966]. It is also given in for example [Martens and Næs 1989 p.111]. NIPALS calculates the principal components one by one, starting from the largest eigenvalue/component. For each component the algorithm uses an iterative approach to calculate the scores and loadings. This "one at a time" approach is useful in spectroscopy, where the data normally is highly redundant, because the redundance implies that the first few principal components often are enough to describe the data almost completely. In other contexts algorithms that calculate all principal components simultaneously can be more useful.

One important feature about PCA is that it do not presuppose any relationship between the variables as traditional statistic models do. Therefore it has no meaning to speak of independent and/or response variables in PCA. PCA is simply a tool for analyzing and describing structures of variation in data sets.

#### Example - NIR and PCA for identifying type of moisture in wood shavings

This example refers to a PCA analysis on near infrared reflectance spectra (1200-2400 nm) of three types of wood shavings: *Fresh shavings* (14 samples), which have a moisture content slightly under that of standing trees, *dry shavings* (9 samples), which are oven dried shavings remoistened to moisture contents below fiber saturation and *wet shavings* (10 samples), which are also oven dried shavings, but remoistened to full water saturation. Typical spectra for the three types of shavings are shown in Figure 9a). There are marked differences in shape. The typical spectrum for the wet shavings has a lower level and less dominant bands than the spectra for the fresh and dry shavings. The fresh and dry shavings differ mainly just in the beginning of the spectra and above approximately 2000 nm. Figure 9b) shows the scores for the first two principal components (factors). These two components explain 99.4 per cent of the variation in the data. The figure shows that factor one holds the difference between the wet shavings and the other two types of shavings, while factor two holds the difference between fresh and dry shavings. The figure also indicates that object W4 is an outlier, since it does not follow the pattern of the other wet shavings. Figure 9c) shows the loadings for factor one and two. It shows that almost all wavelengths contribute equally to factor one, confirming that factor one describes the differences in level between wet shavings and the other two types of shavings. The figure also shows that it is mainly wavelengths just above 1200 nm and above approximately 2000 nm that influence factor two. This stems with the above mentioned about factor two being a factor holding the differences between fresh and dry shavings. Figure 9d) shows the scores for factor one plotted against the scores for factor two. A distinct grouping of the samples is seen, and the outlier (W4) is easy to spot.

**a) Reflectance spectra****b) Scores for factor 1 and 2**

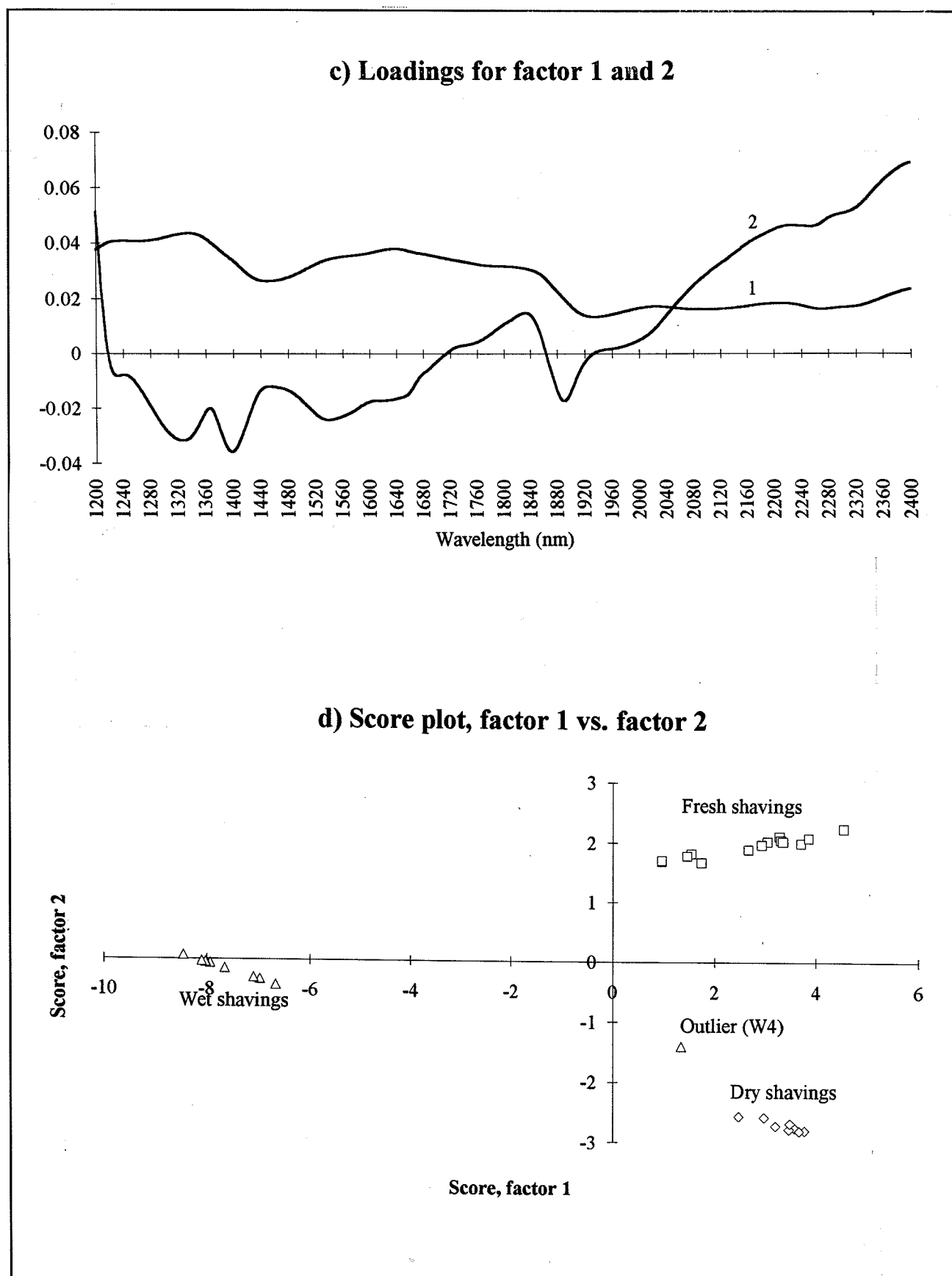


Figure 9. Example of PCA on shavings with different types of moisture content. See text for explanations.

A hypothetical use of the PCA model in this example could be to ascribe unknown samples of shavings to one or none of the three types. Forgetting for a moment that it probably would be more easy just to look at the shape of the spectrum and compare to the known spectra, the procedure in a manual approach would be:

- 1) Multiply the spectrum of the unknown sample with the loading vectors of factor one and two. The result will be one scalar per loading vector, each scalar corresponding to a score, i.e. a coordinate in the plane spanned by the first two score vectors.
- 2) Plot the point in Figure 9d).
- 3) Consider which group the new point belongs to.

If the procedure should be automated, step three needs quantifying. That is: define the borders of the groups and see if the new point is inside any of the groups. A useful tool for defining such borders is Mahalanobis distances, which are described in the next section. It should, however, be noted that PCA is not the best tool for grouping - methods drilled for exactly this application exist [Per Brockhoff, RVAU, pers. com. 1994].

#### *Mahalanobis distances*

A Mahalanobis distance is a distance measure aimed at describing the distance from a point to a cloud of points in a multidimensional space. The Mahalanobis distance takes the variation structure of the point cloud into account so that the unit distance is longer in those directions where the point cloud is oblong. That is, points with the same Mahalanobis distance to a given cloud of points are located on the perimeter of an ellipsoid circumscribing the point cloud, where the direction of the long axis of the ellipsoid is given by the first principal component for the point cloud. According to Mark [1992b] the Mahalanobis distance  $D$  from a point with the position vector  $X$  to the centre  $X_1$  of a point cloud is given by:

$$D^2 = (X - X_1)^T M (X - X_1)$$

where  $M$  is a matrix determining the distance measures. Weisberg [1980] sets  $M$  equal to  $(n-1)(X_0^T X_0)^{-1}$ , where  $n$  is the number of points in the cloud and where  $X_0$  is the centered matrix holding the vectors to the points in the cloud. In this formulation the Mahalanobis distance is a function of the covariance between the points in the cloud.

For qualitative analysis in NIR, the Mahalanobis distances from a new point to the centers of groups of known points in the score space are first calculated. Then the point is ascribed to a group, if the point is closer to the centre of the group than the border of the group, the border being preset to an appropriate value of  $D$ . The number of dimensions in the score space is determined by the appropriate number of principal components, it is not limited to two as in the example in the previous section.

#### **Quantitative analysis**

Quantitative analysis in NIR is to estimate the value of one or more response variables from the spectroscopic measurement of unknown samples. The relationship between response variable and spectroscopic response is established by a calibration model, as described in section 2.1. This section presents the three dominant techniques for multivariate calibration

in NIR: Principal Component Regression (PCR), Partial Least Squares Regression (PLSR) and Artificial Neural Networks (ANN). In the normal versions of the methods, PCR and PLSR both presupposes a linear or nearly linear relationship between the (preprocessed) spectroscopic response and the response variable, while ANN has no such limitations.

#### *Principal component regression (PCR)*

PCR is the regression variant of PCA (described in the section on qualitative analysis). First each spectrum in the calibration set is compressed to a number of scores. Then the response variable is regressed on these scores using MLR. MLR can be used on the scores, because the score vectors are orthogonal, i.e. independent. One can say, that in PCR for NIR, the spectra are compressed to their most dominant dimensions before the response variable is regressed on them.

The model is

$$\mathbf{y} = \mathbf{T}\mathbf{q} + \mathbf{f}$$

where  $\mathbf{y}$  is a  $N \times 1$  column vector holding the reference values of the response variable for the  $N$  objects in the calibration set,  
 $\mathbf{T}$  is a  $N \times A$  matrix holding the  $A$  score vectors,  
 $\mathbf{q}$  is a  $A \times 1$  column vector holding the  $y$ -loadings, i.e. the regression coefficients for the scores estimated by least squares regression of  $\mathbf{y}$  on  $\mathbf{T}$ .  
 $\mathbf{f}$  is a  $N \times 1$  column vector holding the errors, i.e. the differences between  $\mathbf{y}$  and its estimate  $\mathbf{T}\mathbf{q}$ .

When the  $y$ -loadings are found, they can be transformed to regression coefficients (normally denoted  $\mathbf{b}$ ) for the original  $X$ -data, see [Martens & Næs 1989 p.101].

If there are more than one response variable, PCR is equivalent to carrying out one PCR per response variable. The PCA compression will be the same regardless of the response variable, but the  $y$ -loadings will differ.

An important difference between PCR and MLR directly on the variables is that PCR is able to handle collinear data. Another is that in PCR the "independent" (the  $X$ -data) are not assumed to be error free, since one can discard part of the variation in the  $X$ -data during the data compression step (the PCA) by not including the full number of principal components.

Næs et. al [1990] and Næs & Isaksson [1992] demonstrate a calibration method based on PCR called Locally Weighted Regression (LWR). LWR is aimed at giving better predictions by putting more weight on calibration samples that resembles the sample to be predicted than on those that deviate from it. One approach is to measure resemblance as a function of Mahalanobis distances in the principal component score space. LWR is linear, but because the lines are fitted to shorter intervals than in PCR, its potential for modelling non-linear relationships is better.

#### *Partial Least Squares Regression (PLSR)*

PLSR is a bilinear regression method for which the data compression step and the regression step are mixed. That is, the response variable(s) influence(s) the rotation of the loading vectors. Computationally this is accomplished by exchange of scores between the  $X$  and  $Y$ .

matrices during the calculations. One can say that in PLSR for NIR, the spectra are compressed to those dimensions, which are most relevant for the response variables on which they are regressed. By letting the Y loadings influence the X matrix score, the X matrix score vectors will not be orthogonal. However, if so is wished, orthogonal X matrix score vectors can be obtained by extending the algorithm with an extra step and an extra set of loadings, denoted *loading weights*. Algorithms for PLSR regression are presented by Martens & Næs [1989 p.119ff+157]. The algorithms differ in having orthogonal score vectors or not, in the no. of Y variables (the PLS1 algorithm applies for one Y variable, PLS2 for two or more) and in being iterative or non-iterative. An understandable tutorial on PLSR is given by Geladi and Kowalski [1986].

In the form of PLSR normally applied for NIR, the relationship (denoted the inner relation) between the X-matrix score vectors and the Y-matrix score vectors (or the Y-variable itself in the case of only one response variable) is linear. However, Wold [1992] have presented a version of PLSR with spline inner relation. Other modifications also exist.

#### *Artificial Neural Networks (ANN)*

An artificial neural network is a (layered) structure consisting of processing units (nodes) connected by flows of information. The purpose of an ANN is to give certain outputs for certain inputs. The connection between input and output needs not be linear for an ANN to be able to model the connection. One seeks to accomplish the ANN's purpose by presenting the ANN to pairs of corresponding input and desired output and letting it adjust the parameters that influence the flows of information between the nodes until the network gives output acceptably close to the desired. This procedure is called to train the network. In NIR, and other indirect measuring methods, ANN can be used for calibrating instruments. In this case the input is the spectroscopic data and the desired output is the value of the reference. Training the network thus corresponds to calibration. The networks normally used for NIR consists of three layers: an input layer, a hidden layer and an output layer. In the first attempts to adopt ANN to NIR, the whole spectrum was used for input, i.e. one input node per datapoint in the spectrum as described by [Long et al. 1990] and [McClure et al. 1992]. Westerhaus and Reeves [1992] presents an approach where the spectra are first reduced using MPA. However, it has turned out to be more fruitful to compress the spectroscopic data by PCA (or more seldom by PLSR) and then use the scores as input, [Gemperline et al. 1991], [Borggaard & Rasmussen 1992], [Borggaard & Thodberg 1992] and [Kvaal et al. 1992]. Like data for PCR and PLSR, it is sometimes beneficent to preprocess data before presenting it to an ANN. As noted by Borggaard & Thodberg [1992], there is no point in trying too hard to linearize data, as ANN can model non-linear connections. The input variables are normally scaled (for example autoscaled). In cases where the output from the network is scaled, also the response variable is scaled to get comparable numbers. Figure 10 shows the forward flow of information through a small ANN. The input corresponding to one spectrum goes to the units in the input layer, one score  $a_i$  (or variable) per node. The input layer distributes inputs to the hidden layer. Each hidden unit then calculates a weighted sum of the inputs, adds a bias and



transforms the result using a transfer function. Normally a sigmoid function  $f(x)$  is used. [Long et al. 1990] use

$$f(x) = \frac{1}{1 + e^{(-x/\theta)}}$$

where  $\theta$  (the gain) is a parameter influencing the shape of the sigmoid curve. [Borggaard & Thodberg 1992] use

$$f(x) = \frac{1}{(1 - e^{-x}) - 0.5}$$

Each unit in the output layer calculates a weighted sum of the outputs from the hidden layer, adds a bias, and transforms the result using a linear or sigmoid output function. In NIR calibration, the output layer normally consists of only one unit. [Borggaard & Thodberg 1992] also let the output unit receive the output from the input units, so called direct connections. In this way the network also includes linear regression on the PCA scores, ensuring that the net will not do worse than PCR. During training the output is compared to the desired output, and adjustments to the weights and biases are backpropagated through the net. Long et al. [1990] use this formula to calculate the weight adjustment  $\Delta w_{ji}$  to the weight  $w_{ji}$  between unit  $j$  in the hidden layer and unit  $i$  in the input layer:

$$\Delta w_{ji}(n) = \eta \delta_{pj} o_{pi} + \alpha \Delta w_{ji}(n-1)$$

where  $\eta$  is a parameter called the learning rate,  
 $\delta_{pj}$  is the error term for observation (spectrum)  $p$  at the hidden unit  $j$  (the formulation of the error term depends on which output function is used),  
 $o_{pi}$  is the output from input unit  $i$  for observation  $p$ ,  
 $\alpha$  is a parameter called the momentum and were  
 $n$  refers to the present iteration.

In the example given by Borggaard & Thodberg [1992], ANN calibration gave better predictions than PCR and PLSR calibrations.

### Model quality assessment

This section describes how the quality of calibration models is assessed, the quality parameters used and how these parameters are calculated. Lastly, the problem of finding the best calibration is considered.

The benchmark for the quality of a calibration model is its predictive ability for unknown samples belonging to the prediction population. Two things that also contribute to

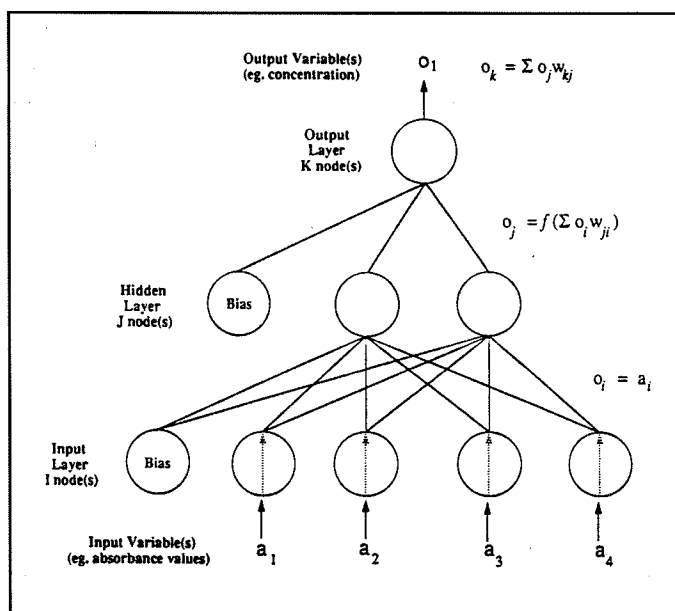


Figure 10. "Schematic representation of a three-layer artificial neural network". Figure and text from [Long et al. 1990].

the quality of a calibration is the structure/complexity of the model and the ability of the calibration system to identify and describe abnormal samples.

### *Predictive ability*

As mentioned in section 2.1, the predictive ability of a model is checked by a validation. That is, the predicted values of the response variable(s) are compared to their actual values as measured by the direct reference method. Validation approaches are cross validation, validation for a test set and leverage correction. An important visual validation is to check the plot of actual values vs. predicted values for the test samples.

In cross validation, one or a few samples are left out, the calibration model is calculated for the rest of the samples and the predictions are compared to the actual value(s) of the left out sample(s). Then another (group of) sample(s) is left out and so on until all samples have been left out once. The form of cross validation where one object a time is left out until all objects have been left out once is denoted full cross validation. The predictive ability validated by cross validation is quantified by the root mean square error of prediction, cross validated *RMSECV*:

$$RMSECV^2 = \frac{\sum_{n=1}^N RMSEP_n^2}{N}$$

where

$$RMSEP_n^2 = \frac{1}{I_p} \sum_{i=1}^{I_p} (y_i - y_{i, pred})^2$$

and where

$N$  is the number of cross validation segments,

$I_p$  is the number of objects per cross validation segment and where

$y_i$  and  $y_{i, pred}$  are the reference value and the predicted value of the response variable for object  $i$ .

When calibrating using a test set, the ability of the model to predict for the test set is quantified by the root mean square error of prediction *RMSEP*. This quantity is calculated by a formula similar to the above given for *RMSEP<sub>n</sub>*. In this case  $I_p$  is the number of objects in the test set. The *RMSECV* and the *RMSEP* can either be given as absolute numbers, as a percentage of the mean value of the reference values for the set of samples or, more seldom, but perhaps more informatively, relative to the standard deviation between the reference values of the (test) set of samples or to the *RMSECV* or *RMSEP* for 0-factor prediction. A quantity often used in connection with *RMSEP* is the standard error of calibration *RMSEC*, which is calculated similar to *RMSEP*, but for the calibration set. *RMSEC* is not a validation quantity. The above described terminology is not the only one in use. In some textbooks and articles  $SEP = RMSEP^2$  and  $SEC = RMSEC^2$  are used, in others *SEP* and *SEC* are used for the quantities, which are here denoted *RMSEP* and *RMSEC*. Sometimes *SEP* is instead called the standard error of performance, and sometimes *SEE*, standard error of estimate is used for what is here called *SEC*. In some software, what is denoted *SEP* is in fact based on both the calibration set and the test set. In short: For every new paper you read/software you use in this

area: check the exact meaning of the *SE* - abbreviations used. A list of various statistical terms and abbreviations, including the above is given by Workman [1992]. Some authors prefer the prediction sum of squares *PRESS* to *RMSECV*. *PRESS* is equal to  $I_p \text{RMSECV}^2$  for full cross validation, i.e. the sum of the squared differences between actual and predicted values for all samples, where predictions are according to models based on all other samples in the set.

A third method sometimes used for "quick and dirty" validation is leverage correction. "Leverage" is explained later, in the subsection on abnormal objects. A model checked by leverage correction is not validated properly, since the method uses the calibration set to simulate prediction errors. This is done by enhancing the differences between the actual and predicted values of the response variable for the calibration through division with the leverage.

In addition to the above, a plot of actual vs. predicted values can be used for visual assessment of the predictive ability. One should especially be aware of any patterns in the residuals. Also the correlation between actual and predicted values can help quantifying the model quality. Useful is also records of how much of the variation in X and Y data the model explains, i.e. an expression of errors and *RMSEP* relative to the variation in the data. Many quantities used in normal regression (e.g. F-values) can be used also for quantifying predictive ability, see [Workman 1992].

### *Model complexity*

The structure/complexity of a model contributes to its quality. For multivariate calibration models complexity is measured in the number of included factors/components/loading vectors. The rule of thumb is: the more simple, the better, as long as the predictive ability is acceptable. The main reason for this is that simple models normally are more robust than complex models, and therefore will give better predictions for unknown samples, i.e. the more complicated, the higher is the risk of overfitting. The other reason is that simple models normally are easier to comprehend and interpret, that is, the structure in the model reflects the structure in the system it describes in an understandable way.

### *Abnormal objects*

The third entity decisive for system quality is the ability to handle abnormal/unusual objects, normally denoted outliers. Outliers can occur both during calibration and prediction, and both in X and Y data. Types of outliers are objects with high residuals and objects with high leverage. The X-residuals are the distances from the points to the hyperspace spanned by the factors, while the Y-residuals are the differences between the actual and predicted values. Leverage is a measure of how much an object (or a variable) potentially influences a model. A definition of leverage  $h_i$  for calibration object  $i$  out of  $I$  objects is given by Martens & Næs [1989 p.276]:

$$h_i = \frac{1}{I} + t_i^T (T^T T)^{-1} t_i$$

where  $T$  is the score matrix for the calibration set and where  $t_i^T$  is the row vector for object  $i$  in this matrix. Thus, leverage is in fact a Mahalanobis distance. If the object is outside the calibration set, the vector  $t_i^T$  holds the scores for the object calculated as the product of the spectrum and the loading vectors for the calibration set. The leverage for an object in the calibration set is between  $1/I$  and 1. A leverage close to 1 indicates high influence on the

model. For objects outside the calibration set the leverage has no upper limit. The general principle in automatic outlier detection is to compare the residual or leverage of an object to the average residual or leverage for the calibration set. A warning is then given if the residual or leverage is greater than the mean value multiplied by some arbitrarily set constant. In multivariate calibration of spectroscopic data the constant is normally set to three, four or five for residuals and to 0.9 for leverage. A useful way of investigating types of outliers is the so called influence plot, in which the residual is plotted against the leverage for each object. An excellent treatment of outlier detection in multivariate calibration is given by Martens & Næs [1989 p.267-296].

### *Finding the best calibration model*

Given that you have chosen the calibration set and test set in a correct way (see section 2.1) and done the measurements, the next problem is how to make the best calibration model based on the available data. Should the spectra be preprocessed? Should PCR, PLSR or ANN be used? How should the model be validated? Which quality parameters should be used? In the case of PCR or PLSR: how many factors should be included? In the case of ANN: which architecture should the net have and what should the parameters be set to? Unfortunately there are no general answers to these questions. The reason for this is that the answers depend on the data and on the aim of the calibration model, i.e. its planned use. One way to handle the problem of finding a good calibration model is to use a two level approach. First there is the question of choosing a calibration method (for example PCR, PLSR or ANN), then there is the question of optimizing the chosen method. On both levels, the choice of quality parameters depends on the intended use of the model. Normally, one would consider the predictive ability important.

One way to settle the first question is to learn from the comparisons already carried out and described in the literature (see for example [Brockhoff *et al.* 1993] and references herein). Be aware of how the comparisons between methods are made (which data set is used - and how, which quality parameters are used, how are the models validated etc.), both when comparing the results of one reference to the results of another reference and when applying the results to your own modelling. Another approach to the question of choosing a method is to try the different methods on the data and choose from the quality of the accomplished models.

The question of optimizing depends on the method chosen. For determining the number of factors in PCR and PLSR models an operational approach exists. It consists of making the model with too many factors, calculate the *RMSEP* or *RMSECV* for each number of factors and then choose the number of factors corresponding to the first local minimum in the test entity. If no minimum is reached, models with too few factors were calculated. The idea behind this approach is to get a simple model with good predictive ability. For training ANN, Borggaard & Thodberg [1992] present an algorithm partly based on trial and error. When trying to optimize an ANN one should be aware of the consequence of the random start weights: probably two networks with the same architecture and the same parameter values will not have identical weights after training, even when trained on the same data set.

For other questions, for example the choice of pretreatment there is p.t. no other way than to use one's knowledge of the data and how they were measured, experience from previous multivariate calibrations and when there is no other way out: trial and error. That is,

look at the model quality parameters in relation to the aim of the calibration and choose the best model. If the comparison does not clearly point to one of the possibilities, the test indicates that the different possibilities are almost equal. In that case the choosing is not crucial, and you can choose any of the possibilities, for example the most simple.

Which ever the chosen strategy, before setting out to find the best calibration model, it is a good idea to set up an algorithm or plan to follow (which preprocessing methods to try, which validation method to use, which quality parameters to attach importance to etc.).

The software available for multivariate calibration is of the GIGO-type (Garbage In, Garbage Out). Hence, the programs are good tools if you have taken the time to study multivariate calibration thoroughly, but as a novice you will soon be frustrated. The programs *will* enable you to produce a dozen different calibration models in very short time, but when it comes to evaluating them relative to each other and choosing the best one, the software will not help you other than by providing the model quality data on which you can base your decision. A hammer is a good tool for the carpenter, but the apprentice is likely to miss the spike and hurt his fingers.

## Appendix B

### Absorption bands in the NIR region

This appendix gives an overview over absorption bands in the NIR region. The first table holds bands assigned by various authors to major wood constituents. The rest of the tables hold tentative general band assignments for organic substances. Be aware of the fact that measurements on which band assignments are based normally are carried out on pure substances, and that bands may shift considerably (tens of nm), when the substance forms part of composites/biological material.

Wood constituent	Absorption bands (nm)
Water (major bands in <i>Italics</i> )	<p>[Williams &amp; Norris 1987]: 834, 938, 958, 978, 986, 994, 1010, 1030, 1099, 1153, <i>1409</i>, <i>1460</i>, 1780, <i>1910</i>, 2305, 2345, 2510</p> <p>[Shenk et al. 1992]: 1940</p> <p>[Andersson &amp; Yngvesson 1992]: 1200, 1430, 1940, 2950</p>
Cellulose (major bands in <i>Italics</i> )	<p>[Williams &amp; Norris 1987]: 860, 905, 920, 978, 1058, 1160, 1190, 1220, 1275, 1363, 1425, 1460, 1520, 1585, 1702, 1825, 2050, 2079, 2103, 2145, 2172, 2268, 2335, 2355, 2370, 2390, 2410, 2445, 2480, 2530, 2560, 2582</p> <p>[Shenk et al. 1992]: 2336</p> <p>[Elvidge 1990]: 1220, 1480, 1930, 2100, 2280, 2340, 2480</p>
Lignin	<p>[Shenk et al. 1992]: 2270</p> <p>[Elvidge 1990]: 1450, 1680, 1930, 2050-2140, 2270, 2330, 2380, 2500</p>
Hemicellulose	<p>[Elvidge 1990], for xylan: 1210, 1450, 1720, 1790, 1930, 2090, 2260, 2330, 2500</p> <p>[Elvidge 1990], for arabinogalactan: 990, 1210, 1450, 1550, 1740, 1930, 2100, 2280, 2320, 2500</p>

The rest of the tables in this appendix are from [Murray & Williams 1987].

Simple Bond Combinations Likely to Cause Absorances  
in Near-Infrared Region

-C-C-	H—O	N-H	-O-H	=P-P	-S-H
C=C	Intramolecular	-NH <sub>2</sub>	-O-O-	=P-C-	-S-S-
-C-H	and	-NH <sub>3</sub>	-O-S-	=P-H	-S-C-
CH <sub>2</sub>	intermolecular	NH <sub>2</sub>	S=O		S=C
-CH <sub>3</sub>	hydrogen	-NH	-O-N=		-S-P=
-CH <sub>2</sub> -phenyl	bonds	-N=N-	O=N-		
-CH=CH <sub>2</sub> vinyl		N-N	-O-C-		
-C-N=		N-P	O=C		
=C=N-		-N=P-	-O-P		
-C=N-		=N-S-	O=P-		
		-N=S-			

Approximate Location of Absorbers Involving Nitrogen and Hydrogen

Wavelength (nm)			Tentative Assignment
1st Overtone	2nd Overtone	3rd Overtone	
	2,540–2,600	1,910–2,080	Amide III: Combination N-H stretch with C-O stretch, secondary amides
		1,950–1,980	Amide III: N-H stretch, <i>trans</i> -secondary amides
	2,330–2,390	1,760–1,800	Amide IV: N-H bend, primary amides
	2,270–2,320	1,710–1,730	N-H bend, <i>cis</i> -secondary amides
	2,200–2,250	1,640–1,680	NH <sub>3</sub> + NH deformation; "amino acid II"
	2,140–2,180	1,600–1,630	N-H bend, <i>trans</i> -secondary amides
	2,050–2,140	1,540–1,600	Ring deformation, pyrimidines, quinolines
	2,080–2,220	1,560–1,670	Amide II: N-H deformation coupled with C-H stretching, secondary amides, especially peptides
	2,040–2,110	1,530–1,580	N=N stretching, unsaturated nitrogen compounds
	2,030–2,100	1,520–1,570	NH <sub>3</sub> deformation; "amino acid I"
	2,020–2,150	1,510–1,610	N-H deformation, primary and secondary amines
1,810–1,970	1,200–1,310		Unknown absorber in most amino acids
1,660–2,500	1,110–1,670	1,000–1,250	N-H stretch, symmetrical, all amino acids and hydrochlorides
1,590–1,650	1,060–1,100		Asymmetrical N-H stretch, all amino acids and hydrochlorides
1,600–1,630	1,070–1,090		N-H stretch, secondary amides, <i>cis</i> and <i>trans</i>
1,570–1,600	1,040–1,060		N-H stretch, secondary amides, <i>cis</i> -bonded NH
1,520–1,620	1,010–1,080		Hydrogen bonding, peptide links, protein helices
1,530–1,580	1,040–1,070		N-H stretch, primary amides, bonded NH
1,500–1,530	1,000–1,020		N-H stretch <i>trans</i> -bonded NH, primary amides
1,510–1,530	1,000–1,020		Unidentified absorber, all proteins
1,490–1,510	–1,000		N-H stretch, imines (e.g., histidine)
1,490–1,510	1,000–1,020		N-H stretch, alkylated primary amines

Approximate Location of C-N Bands in Near-Infrared Region

Wavelength (nm)			Tentative Assignment
1st Overtone	2nd Overtone	3rd Overtone	
		2,420–2,440	C-N stretch, primary-tertiary amines
		2,400–2,420	C-N stretch, primary amines, primary alpha-carbon atoms
		2,310–2,340	C-N stretch, primary amines, primary alpha-carbon atoms
		2,110–2,140	C-N stretch, secondary amines, secondary carbon atoms
	2,480–2,600	1,850–2,000	C-N stretch, acrylamines, alkyl amines, primary-tertiary
	2,450–2,550	1,840–1,870	C-N stretch, <i>cis</i> -secondary amides
	2,340–2,380	1,770–1,800	C-N stretch, amides with no N substitution
	1,970–2,100	1,470–1,570	C-N stretch, unsaturated nitrogen compounds
2,310–2,350	1,540–1,570	1,150–1,170	C-N stretch, -N=C=N-
1,490–1,510	900–1,000	...	C-N stretch, amines

Approximate Location of C-O Bands in Near-Infrared Region

Wavelength (nm)			
1st Overtone	2nd Overtone	3rd Overtone	Tentative Assignment
		2,220-2,380	C-O stretch, primary alcohols
		2,150-2,180	C-O stretch, tertiary alcohols
		2,050-2,100	C-O stretch, phenols
		2,100-2,180	C-O stretch, long-chain fatty acids
	2,590-2,640	1,920-2,080	C-O stretch, amide III combination, secondary amides
	2,330-2,540	1,780-2,080	Coupled C-O and O-H stretch, carboxylic acids
	2,380-2,500	1,780-1,920	C-O symmetrical vibrations, zwitterions
	2,140-2,360	1,600-1,770	C-O stretch, amino acid ionized carbonyls
	1,980-2,220	1,480-1,670	C=O stretch, urea, amide I, especially lower frequencies
	2,070-2,150	1,550-1,620	C-O bending, COO <sup>-</sup> zwitterions
	2,080-2,140	1,560-1,610	C-O stretch, COOH, amino acids
	2,000-2,050	1,510-1,530	C=O stretch, solid primary amines, amide I
	1,990-2,030	1,490-1,520	C=O stretch, internally bonded, saturated aliphatic carboxylic acids
	1,950-1,990	1,460-1,490	C=O stretch, $\alpha$ - $\beta$ unsaturated aldehydes
	1,970-2,080	1,470-1,570	C=O stretch, $\alpha$ - $\beta$ unsaturated ketones
	1,920-1,960	1,440-1,470	C=O stretch, ketones
	1,930-1,970	1,440-1,470	C=O stretch, saturated aliphatic carboxylic acids
	1,910-1,930	1,430-1,450	C=O stretch, saturated aliphatic acids and esters
	1,800-1,920	1,350-1,440	C=O vibrations, open-chain acid anhydrides
2,330-2,420	1,550-1,610	1,160-1,210	COO <sup>-</sup> stretch, or combination band, most amino acids
2,330-2,360	1,530-1,570	1,160-1,180	COO <sup>-</sup> stretch, or combination band ionized amino acids

Approximate Location of O-H Bands in Near-Infrared Region

Wavelength (nm)			
1st Overtone	2nd Overtone	3rd Overtone	Tentative Assignment
		1,950-2,020	O-H deformation, secondary alcohols
	2,330-2,540	1,780-2,080	C-O/O-H stretch coupled, carboxylic acids
	2,510-2,600	1,860-1,900	O-H deformation, primary alcohols
	2,440-2,500	1,820-1,870	O-H deformation, secondary alcohols
	2,000-2,090	1,510-1,540	O-H deformation, hydroxyl
2,060-2,150			C-O, O-H stretching combination, primary alcohols
1,920-1,950			O-H stretch/O-H deformation combination hydroxyl
1,620-1,700	1,110-1,140		O-H stretch, carboxylic acid dimers
1,560-2,000	1,030-1,330		O-H stretch, intramolecular OH bonds, polymers
1,470-1,560	950-1,040		O-H stretch, internal OH bonds, single bridge, polymeric
1,400-1,450			O-H stretch, internal OH bonds, single bridge
1,400-1,430			O-H stretch, COOH groups
1,390-1,420			O-H stretch, intramolecular OH bonds, single bridge
1,380-1,400			O-H stretch, phenols
1,360-1,390			O-H stretch, tertiary alcohols
1,370-1,390			O-H stretch, primary alcohols
1,360-1,380			O-H stretch, secondary alcohols



Approximate Location of C-H Bands in Near-Infrared Region

Wavelength (nm)			
1st Overtone	2nd Overtone	3rd Overtone	Tentative Assignment
	2,460–2,540	2,120–2,150	(CH <sub>3</sub> ) <sub>2</sub> -C; skeletal vibrations
		1,850–2,120	C-H bend, CH in long-chain fatty acids
	2,540–2,580	1,980–2,040	(CH <sub>3</sub> ) <sub>2</sub> -C; skeletal vibrations
	2,460–2,500	1,900–1,940	-CH=CH-; -CH=CH <sub>2</sub> ; CH in phase deformation
	2,410–2,460	1,850–1,880	-CH <sub>2</sub> -; CH deformation
	2,390–2,440	1,820–1,850	-(CH <sub>3</sub> ) <sub>3</sub> ; CH deformations
	2,370–2,400	1,810–1,840	-C(CH <sub>3</sub> ) <sub>3</sub> ; CH deformation
	2,340–2,370	1,770–1,790	C-H in-phase deformation, CHO groups
2,300–2,350		1,750–1,780	-CH=CH <sub>2</sub> in-phase CH <sub>2</sub> deformation
	2,320–2,520		C-H stretching, methylene groups, combination
	2,270–2,300	1,740–1,890	C-H stretch aliphatic compounds
	2,260–2,300	1,710–1,740	C-CH <sub>3</sub> ; CH asymmetrical deformation
	2,190–2,360	1,700–1,730	-CH <sub>2</sub> -; CH asymmetrical deformation
	2,200–2,250	1,640–1,770	Pyrimidines and quinolines, ring deformation
2,140–2,190		1,650–1,680	Benzene rings deformation
2,100–2,200			C-H stretching, <i>cis</i> unsaturation, combination
	2,060–2,150	1,550–1,620	C-H stretching, skeletal in-plane deformation, combination
	2,070–2,100		Benzene rings deformation
	2,020–2,060	1,550–1,580	-C=C- stretch, conjugated chains
		1,510–1,550	-C=C- stretch, nonconjugated chains
1,720–1,860	1,150–1,240		C-H stretch, carbonyl compounds
1,680–1,740	1,120–1,170		C-H stretch, CH <sub>3</sub> groups (A <sub>1</sub> )
1,700–1,760	1,130–1,170		C-H stretch, CH <sub>2</sub> groups (A <sub>2</sub> )
1,700–1,740	1,140–1,160		C-H stretch, -CH= (A <sub>3</sub> )
1,640–1,670	1,090–1,120		-CH=CH-; CH stretch, <i>cis</i> and <i>trans</i>
1,610–1,670	1,090–1,120		C-H stretch, quinolines
1,610–1,660	1,070–1,110		C-H stretch, pyrimidines
1,620–1,650	1,080–1,100		C-H; C-H stretch, aromatics
1,610–1,640	1,070–1,090		C-H stretch, pyridines
1,620–1,640	1,070–1,090		-CH=CH <sub>2</sub> vinyl, C-H stretch

Assignment of Inorganic Absorbers in Near-Infrared Region

Wavelength (nm)			
1st Overtone	2nd Overtone	3rd Overtone	Tentative Assignment
	2,460–2,670	1,480–1,600	P=O free
	2,410–2,500	1,440–1,500	NO <sub>3</sub> <sup>-</sup>
	2,330–2,400	1,390–1,440	NH <sub>4</sub> <sup>+</sup>
	2,290–2,340		P-(phenyl ring)
2,270–2,500	1,510–1,670		C=N, SCN=
	2,230–2,360	1,340–1,420	Carbonates
2,030–2,200	1,350–1,470		P-H stretching
1,850–1,950	1,230–1,300		P-OH stretching
		1,818–2,200	Silicates
		1,810–2,000	Phosphates, PO <sub>4</sub> , all
		1,760–1,860	Sulphates, SO <sub>4</sub> <sup>=</sup>
		1,750–1,900	Phosphates, PO <sub>3</sub> <sup>=</sup>
1,690–1,910	1,130–1,307		-SH stretch (very weak)
		1,600–1,800	P=O hydrogen bonded
		1,600–1,630	NO <sub>2</sub> <sup>-</sup>
1,510–1,650	1,010–1,100	1,510–1,830	Phosphates, PO <sub>2</sub> <sup>-</sup>
			NH <sub>4</sub> <sup>+</sup>